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No. 1545.—JULY 5, 1889.

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY.*

By D. MENDELEEFF, LL.D.,
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NATURE, inert to the eyes of the ancients, has been revealed to us as full of life and activity. The conviction that motion pervaded all things, which was first realised with respect to the stellar universe, has now extended to the unseen world of atoms. No sooner had the human understanding denied to the earth a fixed position and launched it along its path in space, than it was sought to fix immovably the sun and the stars. But astronomy has demonstrated that the sun moves with unswerving regularity through the star-set universe at the rate of about 50 kilometres per second. Among the so-called fixed stars are now discerned manifold changes and various orders of movement. Light, heat, electricity—like sound—have been proved to be modes of motion; to the realisation of this fact modern science is indebted for powers which have been used with such brilliant success, and which have been expounded so clearly at this lecture table by Faraday and by his successors. As in the imagination of Dante, the invisible air became peopled with spiritual beings, so before the eyes of earnest investigators, and especially before those of Clerk-Maxwell, the invisible mass of gases became peopled with particles: their rapid movements, their collisions and impacts became so manifest that it seemed almost possible to count the impacts and determine many of the peculiarities or laws of their collisions. The fact of the existence of these invisible motions may at once be made apparent by demonstrating the difference in the rate of diffusion through porous bodies of the light and rapidly moving atoms of hydrogen, and the heavier and more sluggish particles of air. Within the masses of liquid and of solid bodies we have been forced to acknowledge the existence of persistent though limited motion of their ultimate particles, for otherwise it would be impossible to explain, for example, the celebrated experiments of Graham on diffusion through liquid and colloidal substances. If there were, in our times, no belief in the molecular motion in solid bodies, could the famous Spring have hoped to attain any result by mixing carefully dried powders of potash saltpetre and acetate of soda in order to produce, by pressure, a chemical reaction between these substances through the interchange of their metals, and have derived, for the conviction of the incredulous, a mixture of two hygroscopic though solid salts—nitrate of soda and acetate of potash.

In these invisible and apparently chaotic movements, reaching from the stars to the minutest atoms, there reigns, however, a harmonious order which is commonly mistaken for complete rest, but which is really a consequence of the conservation of that dynamic equilibrium which was first discerned by the genius of Newton, and which has been traced by his successors in the detailed analysis of the particular consequences of the great generalisation, namely, relative immovability in the midst of universal and active movement.

But the unseen world of chemical changes is closely analogous to the visible world of the heavenly bodies, since our atoms form distinct portions of an invisible world, as planets, satellites, and comets form distinct portions of the astronomer's universe; our atoms may therefore be compared to the solar systems, or to the systems of double or of single stars; for example, ammonia (NH_3) may be represented in the simplest manner by supposing the sun nitrogen surrounded by its planets of hydrogen, and common salt (NaCl) may be looked upon as a double star formed of nitrogen and chlorine. Besides, now that the indestructibility of the elements has been acknowledged, chemical changes cannot otherwise be explained than as changes of motion, and the production by chemical reactions of galvanic currents, of light, of heat, of pressure, or of steam power, demonstrate visibly that the processes of chemical reaction are inevitably connected with enormous though unseen displacements, originating in the movements of atoms in molecules. Astronomers and natural philosophers, in studying the visible motions of the heavenly bodies and of matter on the earth, have understood and have estimated the value of this store of energy. But the chemist has had to pursue a contrary course. Observing in the physical and mechanical phenomena which accompany chemical reactions the quantity of energy manifested by the atoms and molecules, he is constrained to acknowledge that within the molecules there exist atoms in motion, endowed with an energy which, like matter itself, is neither being created nor is capable of being destroyed. Therefore, in chemistry we must seek dynamic equilibrium, not only between the molecules, but also in their midst among their competent atoms. Many conditions of such equilibrium have been determined, but much remains to be done; and it is not uncommon, even in these days, to find that some chemists forget that there is the possibility of motion in the interior of molecules, and therefore represent them as being in a condition of death-like inactivity.

* A Lecture delivered at the Royal Institution of Great Britain, May 31, 1889.

Chemical combinations take place with so much ease and rapidity, possess so many special characteristics, and are so numerous, that their simplicity and order was for a long time hid from investigators. Sympathy, relationship, all the caprices or all the fancifulness of human intercourse, seemed to have found complete analogies in chemical combinations, but with this difference, that the characteristics of the material substances—such as silver, for example, or of any other body—remain unchanged in every subdivision from the largest masses to the smallest particles, and consequently their characteristics must be a property of its particles. But the world of heavenly luminaries appeared equally fanciful at man's first acquaintance with it; so much so, that the astrologers imagined a connection between the individualities of men and the conjunctions of planets. Thanks to the genius of Lavoisier and of Dalton, man has been able, in the unseen world of chemical combinations, to recognise laws of the same simple order as those which Copernicus and Kepler proved to exist in the planetary universe. Man discovered, and continues every hour to discover, *what* remains unchanged in chemical evolution, and *how* changes take place in combinations of the unchangeable. He has learnt to predict, not only what possible combinations may take place, but also the very existence of atoms of unknown elementary bodies, and has besides succeeded in making innumerable practical applications of his knowledge to the great advantage of his race, and has accomplished this notwithstanding that notions of sympathy and affinity still preserve a strong vitality in science. At present we cannot apply Newton's principles to chemistry because the soil is only being now prepared. The invisible world of chemical atoms is still waiting for the creator of chemical mechanics. For him our age is collecting a mass of materials, the inductions of well-digested facts, and many-sided inferences similar to those which existed for Astronomy and Mechanics in the days of Newton. It is well also to remember that Newton devoted much time to chemical experiments, and while considering questions of celestial mechanics, persistently kept in view the mutual action of those infinitely small worlds which are concerned in chemical evolutions. For this reason, and also to maintain the unity of laws, it seems to me that we must, in the first instance, seek to harmonise the various phases of contemporary chemical theories with the immortal principles of the Newtonian natural philosophy, and so hasten the advent of true chemical mechanics. Let the above considerations serve as my justification for the attempt which I propose to make to act as a champion of the universality of the Newtonian principles, which I believe are competent to embrace every phenomenon in the universe, from the rotation of the fixed stars to the interchanges of chemical atoms.

In the first place I consider it indispensable to bear in mind that, up to quite recent times, only a one-sided affinity has been recognised in chemical reactions. Thus, for example, from the circumstance that red-hot iron decomposes water with the evolution of hydrogen, it was concluded that oxygen had a greater affinity for iron than for hydrogen. But hydrogen, in presence of red-hot iron scale, appropriates its oyxgen and forms water, whence an exactly opposite conclusion may be formed.

During the last ten years a gradual, scarcely perceptible, but most important change has taken place in the views, and consequently in the researches of chemists. They have sought everywhere, and have always found systems of conservation or dynamic equilibrium substantially similar to those which natural philosophers have long since discovered in the visible world, and in virtue of which the position of the heavenly bodies in the universe is determined. There, where one-sided affinities only were at first detected, not only secondary or lateral ones have been found, but even those which are diametrically opposite; yet among these, dynamical equilibrium establishes itself, not only by excluding one or other of the forces, but regulating them all. So the chemist finds in the flame of the blast furnace, in the formation of every salt, and, with especial clearness, in double salts, and in the crystallisation of solutions, not a fight ending in the victory of one side, as used to be supposed, but the conjunction of forces; the peace of dynamic equilibrium resulting from the action of many forces and affinities. Carbonaceous matters, for example, burn at the expense of the oxygen of the air, yielding a quantity of heat, and forming products of combustion, in which it was thought that the affinities of the oxygen with the combustible elements were satisfied. But it appeared that the heat of combustion was competent to decompose these products, to dissociate the oxygen from the combustible elements, and therefore to explain combustion fully it is necessary to take into account the equilibrium between opposite reactions, between those which evolve and those which absorb heat.

In the same way, in the case of the solution of common salt in water, it is necessary to take into account, on the one hand, the formation of compound particles generated by the combination of salt with water, and on the other, the disintegration or scattering of the new particles formed, as well as of those originally contained. At present we find two currents of thought, apparently antagonistic to each other, dominating the study of solutions: according to the one, solution seems a mere act of building up or association; according to the other, it is only dissociation or disintegration. The truth lies evidently between these views; it lies, as I have endeavoured to prove by my investigations into aqueous solutions, in the dynamic equilibrium of particles tending to combine and also to fall asunder. The large majority of chemical reactions which appeared to act victoriously along one line have been proved capable of acting as victoriously even along an exactly opposite line. Elements which utterly decline to combine directly may often be formed into comparatively stable compounds by indirect means, as, for example, in the case of chlorine and carbon; and consequently the sympathies and antipathies, which it was thought to transfer from human relations to those of atoms, should be laid aside until the mechanism of chemical relations is explained. Let us remember, however, that chlorine, which does not form with carbon the chloride of carbon, is strongly absorbed or, as it were, dissolved by carbon, which leads us to suspect incipient chemical action, even in an external and purely surface contact, and involuntarily gives rise to conceptions of that unity of the forces of nature which has been so energetically insisted on by Sir William Grove, and formulated in his famous paradox. Grove noticed that platinum, when fused in the oxyhydrogen flame, during which operation water is formed, when allowed to drop into water decomposes the latter and produces the explosive oxyhydrogen mixture. The explanation of this paradox, as of many others which arose during the period of chemical renaissance, has led, in our time, to the promulgation by Henri Ste. Claire Deville of the conception of dissociation and of equilibrium, and has recalled the teaching of Berthollet, which, notwithstanding its brilliant confirmation by Heinrich Rose and Dr. Gladstone, had not, up to that period, been included in received chemical views.

Chemical equilibrium in general, and dissociation in particular, are now being so fully worked out in detail, and applied in such various ways, that I do not allude to them to develop, but only use them as examples by which to indicate the correctness of a tendency to regard chemical combinations from points of view differing from those expressed by the term hitherto appropriated to define chemical forces, namely, "affinity." Chemical equilibria, dissociation, the speed of chemical reactions, thermochemistry, spectroscopy, and, more than all, the determination of the influence of masses and the search for a connection between the properties and weights of atoms and molecules; in one word, the vast mass of the most

important chemical researches of the present day, clearly indicates the near approach of the time when chemical doctrines will submit fully and completely to the doctrine which was first announced in the Principia of Newton.

In order that the application of these principles may bear fruit it is evidently insufficient to assume that statical equilibrium reigns alone in chemical systems or chemical molecules: it is necessary to grasp the conditions of possible states of dynamical equilibria, and to apply to them kinetic principles. Numerous considerations compel us to renounce the idea of statical equilibrium in molecules, and the recent yet strongly supported appeals to dynamic principles constitute, in my opinion, the foundation of the modern teaching relating to atomicity, or the valency of the elements, which usually forms the basis of investigations into organic or carbon compounds.

This teaching has led to brilliant explanations of very many chemical relations and to cases of isomerism, or the difference in the properties of substances having the same composition. It has been so fruitful in its many applications and in the foreshadowing of remote consequences, especially respecting carbon compounds, that it is impossible to deny its claims to be ranked as a great achievement of chemical science. Its practical application to the synthesis of many substances of the most complicated composition entering into the structure of organised bodies, and to the creation of an unlimited number of carbon compounds, among which the colours derived from coal-tar stand prominently forward, surpass the synthetical powers of Nature itself. Yet this teaching, as applied to the structure of carbon compounds, is not, on the face of it, directly applicable to the investigation of other elements, because, in examining the first, it is possible to assume that the atoms of carbon have always a definite and equal number of affinities, while in the combinations of other elements this is evidently inadmissible. Thus, for example, an atom of carbon yields only one compound with four atoms of hydrogen and one with four atoms of chlorine in the molecule, while the atoms of chlorine and hydrogen unite only in the proportions of one to one. Simplicity is here evident, and forms a point of departure from which it is easy to move forward with firm and secure tread. Other elements are of a different nature. Phosphorus unites with three and with five atoms of chlorine, and consequently the simplicity and sharpness of the application of structural conceptions are lost. Sulphur unites only with two atoms of hydrogen, but with oxygen it enters into higher orders of combination. The periodic relationship which exists among all the properties of the elements, such, for example, as their ability to enter into various combinations, and their atomic weights, indicate that this variation in atomicity is subject to one perfectly exact and general law, and it is only carbon and its near analogues which constitute cases of permanently preserved atomicity. It is impossible to recognise as constant and fundamental properties of atoms, powers which, in substance, have proved to be variable. But, by abandoning the idea of permanence, and of the constant saturation of affinities—that is to say, by acknowledging the possibility of free affinities—many retain a comprehension of the atomicity of the elements "under given conditions"; and on this frail foundation they build up structures composed of chemical molecules, evidently only because the conception of manifold affinities gives, at once, a simple statical method of estimating the composition of the most complicated molecules.

I shall enter neither into details, nor into the various consequences following from these views, nor into the disputes which have sprung up respecting them (and relating especially to the number of isomers possible on the assumption of free affinities), because the foundation or origin of theories of this nature suffers from the radical defect of being in opposition to dynamics. The molecule, as even Laurent expressed himself, is represented as an architectural structure, the style of which is determined by the fundamental arrangement of a few atoms, while the decorative details, which are capable of being varied by the same forces, are formed by the elements entering into the combination. It is on this account that the term "structural" is so appropriate to the contemporary views of the above order, and that the "constructors" seek to justify the tetrahedric, plane, or prismatic disposition of the atoms of carbon in benzole. It is evident that the consideration relates to the statical position of atoms and molecules and not to their kinetic relations. The atoms of the structural type are like the lifeless pieces on a chess board: they are endowed but with the voices of living beings, and are not those living beings themselves; acting, indeed, according to laws, yet each possessed of a store of energy, which, in the present state of our knowledge, must be taken into account.

In the days of Haüy, crystals were considered in the same statical and structural light, but modern crystallographers, having become more thoroughly acquainted with their physical properties and their actual formation, have abandoned the earlier views and have made their doctrines dependent on dynamics.

The immediate object of this lecture is to show that, starting with Newton's third law of motion, it is possible to preserve to chemistry all the advantages arising from structural teaching, without being obliged to build up molecules in solid and motionless figures, or to ascribe to atoms definite limited valencies, directions of cohesion, or affinities. The wide extent of the subject obliges me to treat only a small portion of it, namely, of *substitutions*, without specially considering combinations and decompositions, and, even then, limiting myself to the simplest examples, which, however, will throw open prospects embracing all the natural complexity of chemical relations. For this reason, if it should prove possible to form groups similar, for example, to H_4 or CH_6 as the remnants of molecules CH_4 or C_2H_6 we shall not pause to consider them, because, as far as we know, they fall asunder into two parts, H_2+H_2 or CH_4+H_2, as soon as they are even temporarily formed, and are capable of separate existence, and therefore can take no part in the elementary act of substitution. With respect to the simplest molecules which we shall select—that is to say, those of which the parts have no separate existence, and therefore cannot appear in substitutions—we shall consider them according to the periodic law, arranging them in direct dependence on the atomic weight of the elements.

Thus, for example, the molecules of the simplest hydrogen compounds—

HF	H_2O	H_3N	H_4C
hydrofluoric acid	water	ammonia	methane

correspond to elements the atomic weight of which decrease consecutively,

$$F = 19, O = 16, N = 14, C = 12.$$

Neither the arithmetical order (1, 2, 3, 4 atoms of hydrogen) nor the total information we possess respecting the elements will permit us to interpolate into this typical series one more additional element; and therefore we have here, for hydrogen compounds, a natural base upon which are built up those simple chemical combinations which we take as typical. But even they are competent to unite with each other, as we see, for instance, in the property which hydrofluoric acid has of forming a hydrate, that is of combining with water; and the similar attribute of ammonia, resulting in the formation of a caustic alkali, NH_3H_2O, or NH_4OH.

Having made these indispensable preliminary observations, I may now attack the problem itself and attempt to explain the so-called structure, or rather construction of molecules, that is to say, their constitution and transformations, without having recourse to the teaching of "structionists," but on Newton's dynamical principles.

Of Newton's three laws of motion, only the third can be applied directly to chemical molecules when regarded

as systems of atoms among which it must be supposed that there exist common influences or forces, and resulting compounded relative motions. Chemical reactions of every kind are undoubtedly accomplished by changes in these internal movements, respecting the nature of which nothing is known at present, but the existence of which, the mass of evidence collected in modern times, forces us to acknowledge as forming part of the common motion of the universe, and as a fact further established by the circumstance that chemical reactions are always characterised by changes of volume or the relations between the atoms or the molecules. Newton's third law, which is applicable to every system, declares that, "action is always associated with reaction, and is equal to it." The brevity and conciseness of this axiom was, however, qualified by Newton in a more expanded statement, "the action of bodies one upon another is always equal, and in opposite directions." This simple fact constitutes the point of departure for explaining dynamic equilibrium, that is to say, systems of conservancy. It is capable of satisfying even the dualists, and of explaining, without additional assumptions, the preservation of those chemical types which Dumas, Laurent, and Gerhardt created unit types, and those views of atomic combinations which the structionists express by atomicity or the valency of the elements, and, in connection with them, the various numbers of affinities. In reality if a system of atoms or a molecule be given, then in it, according to the third law of Newton, each portion of atoms acts on the remaining portion in the same manner, and with the same force as the second set of atoms acts on the first. We infer directly from this consideration that both sets of atoms, forming a molecule, are not only equivalent with regard to themselves, as they must be according to Dalton's law, but also that they may, if united, replace each other. Let there be a molecule containing atoms A B C, it is clear that, according to Newton's law, the action of A on B C must be equal to the action of B C on A, and if the first action is directed on B C, then the second must be directed on A, and consequently then, where A can exist in dynamic equilibrium, B C may take its place and act in a like manner. In the same way the action of C is equal to the action of A B. In one word, every two sets of atoms forming a molecule are equivalent to each other, and may take each other's place in other molecules, or, having the power of balancing each other, the atoms or their complements are endowed with the power of replacing each other. Let us call this consequence of an evident axiom "the principle of substitution," and let us apply it to those typical forms of hydrogen compounds, which we have already discussed, and which, on account of their simplicity and regularity, have served as starting points of chemical argument long before the appearance of the doctrine of structure.

In the type of hydrofluoric acid, HF, or in systems of double stars, are included a multitude of the simplest molecules. It will be sufficient for our purpose to recall a few: for example the molecules of chlorine, Cl_2, and of hydrogen, H_2, and hydrochloric acid HCl, which is familiar to all in aqueous solution as spirit of salt, and which has many points of resemblance with HF, HB_2, HI. In these cases division into two parts can only be made in one way, and therefore the principle of substitution renders it probable that exchanges between the chlorine and the hydrogen can take place, if they are competent to unite with each other. There was a time when no chemist would even admit the idea of any such action; it was then thought that the power of combination indicated a polar difference of the molecules in combination, and this thought set aside all idea of the substitution of one component element by another.

Thanks to the observations and experiments of Dumas and Laurent fifty years ago, such fallacies were dispelled, and in this manner, this same principle of substitution was exhibited. Chlorine and bromine acting on many hydrogen compounds, occupy immediately the place of their hydrogen, and the displaced hydrogen, with another atom of chlorine or bromine, forms hydrochloric acid or bromide of hydrogen. This takes place in all typical hydrogen compounds. Thus chlorine acts on this principle on gaseous hydrogen —reaction, under the influence of light, resulting in the formation of hydrochloric acid. Chlorine acting on the alkalies, constituted similarly to water, and even on water itself—only, however, under the influence of light, and only partially because of the unstability of HClO—forms by this principle bleaching salts, which are the same as the alkalies, but with their hydrogen replaced by chlorine. In ammonia and in methane, chlorine can also replace the hydrogen. From ammonia is formed in this manner the so-called chloride of nitrogen, NCl_3, which decomposes very readily with violent explosion on account of the evolved gases, and falls asunder as chlorine and nitrogen. Out of marsh gas, or methane, CH_4, may be obtained consecutively, by this method, every possible substitution, of which chloroform, $CHCl_3$, is the best known, and chloro-carbonic acid, CCl_4, the most instructive. But by virtue of the fact that chlorine and bromine act, in the manner shown, on the simplest typical hydrogen compounds, their action on the more complicated ones may be assumed to be the same. This can be easily demonstrated. The hydrogen of benzole, C_6H_6, reacts feebly under the influence of light on liquid bromine, but Gustavson has shown that the addition of the smallest quantity of metallic aluminium causes energetic action, and the evolution of large volumes of bromide of hydrogen.

If we pass on to the second typical hydrogen compound, that is to say water, its molecule, HOH, may be split up in two ways: either into an atom of hydrogen and a molecule of oxide of hydrogen, HO, or into oxygen, O, and two atoms of hydrogen, H; and therefore, according to the principle of substitution, it is evident that one atom of hydrogen can exchange with oxide of hydrogen, HO, and two atoms of hydrogen, H, with one atom of oxygen, O.

Both these forms of substitution will constitute methods of oxidation, that is to say, of the entrance of oxygen into the compound—a reaction which is so common in nature as well as in the arts, taking place at the expense of the oxygen of the air or by the aid of various oxidising substances or bodies which part easily with their oxygen. There is no occasion to reckon up the unlimited number of cases of such oxidising reactions. It is sufficient to state that in the first of these oxygen is directly transferred, and the position, the chemical function, which hydrogen originally occupied is, after the substitution, occupied by the hydroxyl. Thus ammonia, NH_3, yields, hydroxylamine, $NH_2(OH)$, a substance which retains many of the properties of ammonia.

Methane and a number of other hydrocarbons yield, by substitution of the hydrogen by its oxide, methylic, $CH_3(OH)$, and other alcohols. The substitution of one atom of oxygen for two atoms of hydrogen is equally common with hydrogen compounds. By this means alcoholic liquids containing ethyl alcohol, or spirits of wine, $C_2H_5(OH)$, are oxidised till they become vinegar or acetic acid, $C_2H_3O(OH)$. In the same way caustic ammonia, or the combination of ammonia with water, NH_3H_2O, or $NH_4(OH)$, which contains a great deal of hydrogen, by oxidation exchanges four atoms of hydrogen for two atoms of oxygen, and become converted into nitric acid, $NO_2(OH)$. This process of conversion of ammonia salts into saltpetre goes on in the fields every summer, and with especial rapidity in tropical countries. The method by which this is accomplished, though complex, though involving the agency of all-permeating micro-organisms, is, in the substance, the same as that by which alcohol is converted into acetic acid, or glycol, $C_2H_4(OH)_2$, into oxalic acid, if we view the process of oxidation in the light of the Newtonian principles.

(To be continued).

A VOLUMETRIC METHOD FOR THE ESTIMATION OF FAT IN MILK.

By G. E. PATRICK.

A METHOD which I have recently devised for the rapid estimation of fat in milk, consists in bringing all the milk solids, excepting fat, into acid solution in a solvent which is without sensible action upon the fat, and then measuring the latter at a fixed temperature in a narrow calibrated tube.

The solvent which I use is a mixture of strong acetic acid (80 per cent or upwards in strength), oil of vitriol, and concentrated hydrochloric acid, in about the proportions of 9, 5, and 2 by volume. The HCl is added after the mixture of the other two is cooled. These proportions may be varied considerably without much impairing the efficiency of the solvent. Thus, mixtures of 9, 4, and 4 volumes respectively, and even of 9, 3, and 3, have given good results ; but the first-mentioned mixture effects solution quicker, gives fully as clear a solution, and, I have frequently thought, leaves less fat adhering to the walls of the tube as it (the fat) subsides to its place for measurement. Even a mixture of acetic and hydrochloric or of acetic and sulphuric, in the proportions of 9 to 5 or 6 by volume, does fairly well, but neither is as satisfactory as a mixture of the three.

It also seems worth recording that any material increase in the amount of HCl in the various mixtures named results in more or less turbidity of the milk solution, and thereby renders somewhat difficult the accurate reading of the fat. If from any cause this turbidity ever appears it can be avoided in a second trial by simply increasing the proportion of acetic acid, making a mixture of about 11, 5, and 2 volumes respectively. The increase of acetic acid retards somewhat the solvent action, while giving a lighter coloured and clearer solution of the milk solids.

The proportion of the solvent to the milk analysed may also be varied considerably without affecting the final results. I take usually 10·8 c.c. milk and 15 c.c. of the solvent. The operation is performed in a tube about 30 c.m. long, of about 17 m.m. calibre, excepting for a distance of 7 or 8 c.m. near the middle, where it is reduced to a thick-walled tube of about 5 m.m. calibre. The low part or body of the tube holds 21 to 22 c.c., and when charged the liquid fills the narrow portion and reaches about 2 c.m. above it. By means of a lateral perforation in the body of the tube, kept closed by a rubber band (a section of tubing) also perforated, the latter perforation being a little to one side of the former, using a pin as a lever, the liquid may be gradually withdrawn, and the fat made to enter the narrow part, which is graduated in divisions of 0·025 c.c. each. If 10·8 c.c. of milk are taken one such division = 0·2 per cent of fat, measured at 60° C., assuming average densities for both milk and fat. Of course any other scale and any other charge of milk may be employed, provided the tube be correctly proportioned. Before charging the tube there are placed in its lower part (best enclosed there when the tube is made) two pieces of pumice stone joined together by a bit of platinum wire, a very effective combination proposed by Dr. G. C. Caldwell, to promote the regular boiling of liquids. In charging the tube the milk is first pipetted in, half or more of the required acid mixture is then added and well shaken with it, and the remainder then poured in—or a quantity sufficient to bring the liquid to the proper height in the tube. The charged tube is placed on a sand-bath, its contents heated to boiling, boiled quite briskly for ten minutes, then rather gently for ten minutes, or longer if necessary, in order to collect the fat in a layer at the top, and keep it gently agitated with an up-and-down motion until perfectly clear. A little practice is required to learn how best to manage the heat in this latter stage of boiling. When the fat layer is perfectly clear the tube is immediately placed in water at 60° C. for ten minutes, and if great accuracy is not required the fat is at once lowered into the graduated tube, and its volume read at 60° after re-immersion in the water for a few moments. In the descent a little fat usually adheres to the tube, making the reading low by 0·05 to 0·2 per cent. Therefore, for exact results, the column of fat is only lowered until its top is just above that of the graduated tube ; with a few drops of ether the adhering fat is washed down, the tube is replaced in hot water until the ether is *entirely* expelled, after which the fat is lowered and read at 60° C.

Results agree well with those by the Adams process as modified by Thompson* (filter-paper instead of blotting-paper), seldom differing from them by more than 0·1 per cent on samples of mixed milk.

The process has not yet been tested on milk from individual cows, all tests thus far having been on the mixed milk from a herd of thirty.

The process is very expeditious ; with a little practice one can make three or four determinations, side by side, in an hour and a half.

Agricultural Experiment Station, Ames, Iowa,
June 13, 1889.

THE ACTION OF SILICON ON THE METALS GOLD, SILVER, PLATINUM, AND MERCURY.

By H. N. WARREN, Research Analyst.

WITH regard to the action of silicon on the more common metals, iron and copper, so well known are the properties in general of these elements when combined, that little, if any, comment is required; but on passing to the more refractory metals a much wider field for study is presented.

As recorded by the various handbooks of chemistry, silicon, when in the nascent state, converts platinum into a brittle silicide. This is by no means, however, the only method available for preparing this compound; for, on heating graphitoidal silicon in contact with platinum to a full red heat, combination at once takes place, resulting in a brittle regulus, being fusible at a red heat, and breaking with a crystalline fracture, at the same time being difficultly soluble in acids. The same compound may be more readily formed by heating in a closed crucible a mixture of amorphous silicon and platinum black under a layer of potassium silico-fluoride, the analysis of several results thus obtained proved the presence of 10 per cent silicon. On the other hand, neither silver or gold present any great affinity towards silicon, but on heating a mixture of potassium silico-fluoride, metallic sodium, and either silver or gold in the amorphous condition to a high temperature, a well-fused regulus of silicide of the metal may be obtained. In the latter instance, the alloy, containing as little as 5 per cent silicon, is almost as brittle as antimony, and, to all appearances, resembles gold alloyed with a due proportion of silver. At the same time, although silicon possesses no considerable affinity towards either gold or silver, except when in a nascent state, still that affinity appears to be considerably enhanced by combining with either metal, when in the fused condition, a small quantity of an already prepared silicide of either gold, silver, or platinum. Thus, if on to the surface of a quantity of either silver or gold in the fused condition is ejected a few grains of an already prepared silicide of either gold or silver, complete mixture of the same at once ensues. This alloy, although containing but a minute percentage of silicon, may be raised to a much higher rate by the introduction of elementary silicon, which, before this period, showed at all normal temperatures no great affinity, except when in a nascent form ;

* *Analyst*, 1886, p. 73.

silver when thus impregnated with from 10 per cent of silicon, becomes of a slightly red tint, resembling in appearance metallic manganese. The regulus, after being pulverised, being completely decomposed by the aid of concentrated hydriodic acid.

As regards the action of silicon on metallic mercury nothing very definite can at present be stated, but on subjecting a small vessel containing mercury in contact with an alcoholic solution of silicon fluoride to the action of a powerful battery, and afterwards subjecting the mercury to distillation, a small quantity of amorphous silicon was obtainable, but whether silicon, when in a nascent state, combines with or is soluble in mercury, still presents considerable doubt.

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ZIRCONIUM AND ITS ATOMIC WEIGHT.*

By G. H. BAILEY, D.Sc., Ph.D., The Owens College.

THE investigation described in the following paper was undertaken primarily with a view to the re-determination of the atomic weight of zirconium. In previous determinations the sulphate had been used by Berzelius (*Poggendorff Annalen*, vol. iv., p. 126) and Mats Weibull ("Om Zirkonium och dess föreningar"), the chloride and oxychloride by Hermann (*Journ. Prakt. Chem.*, vol. xxxi., p. 77), and the double fluoride of potassium and zirconium by Marignac (*Annales de Chimie*, vol. lx., 1860, p. 270). The results of these determinations are summed up in the following table, the relation O : H = 15·96 : 1 being used in the calculations.

	Mean determination.	Maximum.	Minimum.	Author.
$Zr(SO_4)_2 : ZrO_2$	89·23	89·42	89·05	Berzelius.
$Zr(SO_4)_2 : ZrO_2$	89·255	90·158	88·97	Mats Weibull.
$Zr : Cl_4$	88·56	—	—	Hermann.
$ZrO_2 : HCl$	89·915	90·76	89·07	,,
$K_2ZrF_6 : K_2SO_4$	90·31	92·57	89·84	Marignac.
$ZrO_2 : K_2SO_4$	90·47	90·97	90·02	,,
$K_2ZrF_6 : ZrO_2$	90·6	91·1	89·7	,,

The sulphate is somewhat readily decomposed by heat, the chloride and oxychloride are known to be unstable, and liable to considerable variation of composition according to the method of preparation, and the conditions under which these variations of composition are brought about were not understood, except in so far as the researches of Troost and others have indicated the great tendency which the salts show to pass into volatile and non-volatile oxychlorides of complicated character.

The determination is rendered difficult and unsatisfactory in consequence of—

(*a*). The difficulty of obtaining pure zirconia, and its separation from iron, titanium, and from silica.

(*b*). The tendency to form basic salts, and the hygroscopic character of its salts, and their general instability.

(*c*). The tenacity with which the hydrated zirconia retains the alkalies and smaller quantities of impurities in general.

Under these circumstances it seemed to me essential that any determination of the atomic weight of this element should be preceded by an inquiry into the best method of preparing pure zirconia, and an examinaton of the salts which might be made use of for the purpose, especially with reference to their stability.

Preparation of Crude Zirconia.

The raw material consisted of about 300 grms. of zircons from North Carolina, for whlch I was indebted to the kindness of Sir Henry Roscoe, and in addition to this a quantity of impure zirconia. The zircons were powdered by heating them to redness, and then throwing them quickly into cold water; they were then roughly powdered in an iron mortar, and finally in an agate mortar, and passed through linen. Part of this was treated with hydrogen potassium fluoride, the product being extracted with water, and re-crystallised many times from hot water. Prepared in this way, however, the zirconia was still impure, and showed the presence of iron in small quantities, and in addition to this it was extremely difficult to get rid of alkali.

The methods of fusion with sodium carbonate or acid potassium sulphate are troublesome and even less satisfactory.

Ultimately caustic soda and sodium fluoride were adopted for breaking up the zircons as recommended by Linnemann, and a modified form of the process followed out by him (*Monatsh. f. Chem.*, vol. vi., p. 337) was adopted as the most convenient. A mixture of 100 grms. of caustic soda and 10 grms. of sodium fluoride is heated in a covered silver dish over a large Bunsen burner, 25 grms. of finely powdered zircons are added in portions, the melt being kept stirred, and the heating continued for about an hour, or so long as there is any effervescence. The resulting mass is broken up and extracted with water, the residue consisting principally of sodium zirconate, but containing also silica and undecomposed zircon, oxide of iron, &c. This is now digested with dilute hydrochloric acid and filtered, the residue being subjected repeatedly to the same treatment. The acid solution containing the zirconium is evaporated to perfect dryness, and then exhausted with very dilute hydrochloric acid, and the silica filtered off. The process of solution and evaporation is repeated until the residue obtained dissolves completely in the acid. The impurity now present in the largest quantity is iron, and it was thought desirable to remove the bulk of this first. The hydrochloric acid solution is, therefore, evaporated to small bulk, and left to cool; the oxychloride of zirconium separates out in acicular crystals, leaving the iron in solution. The crystals are thrown into a funnel, and the liquid as far as possible removed at the pump, and the process of solution and separation of crystals in this way repeated several times. On precipitation of the final products with ammonia the crude zirconia is obtained, which forms the starting-point for further purification. In further operations, reagents (such as potassium or sodium salts) which could not be removed by volatilisation were avoided, and even at the present stage it was found necessary to re-dissolve the zirconia in hydrochloric acid, and re-precipitate with ammonia three times before the bulk of the sodium salts were got rid of.

Purification of the Crude Zirconia.

This crude zirconia, free from the impurities that occur in larger quantity, was dissolved in hydrochloric acid, and crystallised out as oxychloride. The aqueous solution of this, slightly acidulated, was treated with sulphuretted hydrogen for twenty-four hours; a gelatinous precipitate was obtained of a purplish black colour, consisting principally of sulphides of silver and copper, together with some hydrated zirconia. To the filtrate saturated with sulphuretted hydrogen was now added a little ammonia, which had the effect of bringing down a little more zirconia, and also small quantities of impurities precipitable by ammonium sulphide. The liquid was now acidulated and boiled down to get rid of the sulphuretted hydrogen, and excess of oxalic acid added to the concentrated solution to precipitate gadolinite earths, and finally treated with ammonium oxalate. There still remained some iron which had either not been removed or had been introduced in the course of treatment. To separate this, the oxychloride was crystallised repeatedly from concentrated hydrochloric acid, and finally washed with a mixture of the acid with one part of alcohol

* A Paper read before the Royal Society, May 9, 1889.

and ten parts of ether. The only impurity that could now be detected was soda, which the zirconia retained with the greatest tenacity.

This was removed by precipitating the zirconia several times by means of ammonia, and re-dissolving it in hydrochloric acid. The zirconia finally precipitated by ammonia was washed* so long as any ammonium salts could be detected in the wash water.

The zirconia obtained was tested as to purity in the following way:—

(1). A portion treated with hydrofluoric acid showed no alteration in weight.

(2). The moist oxide dissolved completely in oxalic acid.

(3). On ignition it was perfectly white (inclined to a bluish cast), and a quantity exhausted with hydrochloric showed no trace of iron by the most delicate tests.

In order, however, to have a further guarantee that the product used for the determination of atomic weight had a definite composition and character, the experiments described later for the determination of atomic weight were made upon four portions, whose final treatment was as essentially different as possible.

Portion A was precipitated from an acid solution of the sulphate by the addition of hydrogen peroxide containing no other impurity than sulphuric acid.

Portion B was transformed into the tetrachloride by heating the zirconia with charcoal in a current of chlorine and then re-precipitating by ammonia.

Portion C was crystallised out from concentrated sulphuric acid by boiling off part of the excess of acid and then allowing to cool.

Portion D was further re-crystallised from hydrochloric acid, and washed very thoroughly with a mixture of hydrochloric acid, alcohol, and ether as described.

Stability of the Zirconium Salts.

In the case of zirconium it was evident that the number of compounds of a simple character and of sufficient stability to afford a good basis for a determination of atomic weight must be very limited. The principles, therefore, on which it was decided to proceed were—

(*a*). To prepare zirconia by several independent methods.

(*b*). To ascertain the most stable salt (or salts if more than one should prove stable), and the most simple transformation of this which would lead to an accurate determination.

Indeed, it seems to me in general that unless there are two or more salts of a very stable character, that reliance should lean rather towards the production of the raw material by independent processes, than towards the confirmation of results obtained from a more stable salt by means of values derived from observations on one that is less stable.

The methods previously used in the determination involved—

(1). Relation of zirconium sulphate to oxide.

(*a*). Direct conversion by ignition.

(*b*). *Viâ* $BaSO_4$ by precipitation.

Mats Weibull (*loc. cit.*); Berzelius (*Pogg. Ann.*, vol. iv., p. 126).

(2). Relation of Zr (as ZrO_2) to Cl (as AgCl).

(*a*). By analysis of $ZrCl_4$.

(*b*). By analysis of $ZrOCl_2$.

Hermann (*Journ. Pr. Chem.*, vol., 97, p. 323).

(3). Relation of K_2ZrF_6 to ZrO_2 and to K_2SO_4. Marignac (*Ann. de. Chim.*, vol. lx., p. 257).

In addition to these it seemed possible that the relations—

(4). Zr to ZrO_2 by direct oxidation of the metal.

(5). Zr (as ZrO_2) to Br (as AgBr) on analysis of $ZrBr_4$, might be worthy of examination.

The bodies, therefore, to be investigated were the metal, the oxide, the chloride, the oxychloride, bromide, sulphate, and double fluoride. With regard to the last mentioned, no further investigation was considered necessary after the very complete treatment it has received at the hands of Marignac following upon the work of Berzelius on the double fluorides.

Preparation and Properties of Zirconium.

Zirconium was first obtained by Berzelius (*Poggendorff Annalen*, vol. iv., p. 117) by heating the anhydrous potassium zirconium fluoride with metallic potassium in an iron tube. It is described by him as being an amorphous black powder without lustre, and resembling charcoal in appearance. Becquerel, by electrolysis of a concentrated solution of the oxychloride, and Troost (*Journ. Prakt. Chem.*, vol. xcvii., p. 171), by fusing together potassium zirconium fluoride and aluminium, obtained it in a crystalline form, though it does not seem to have been in either case quite pure. Phipson (*Journ. Prakt. Chem.*, vol. xcvi., p. 447) found that, like carbon, boron, and silicon, it can be obtained by heating together magnesium and zirconia and then extracting the excess of magnesium and the magnesia by means of dilute hydrochloric acid.

There was left a black amorphous powder resembling that described by Berzelius. No determinations are, however, given to show how far this was free from impurity, and whether it contained unreduced oxide. A repetition of Phipson's experiments showed that, as far as the presence of foreign impurity is concerned, it leaves nothing to be desired, though I have not succeeded in preparing the metal by this or any other of the methods in a state of sufficient purity for a determination of atomic weight. Phipson's method is a very convenient one for preparing the metal, and the following results will show the conditions most favourable to its production in this way.

Experiments were first tried with intimate mixtures of magnesium powder, 3 grms. and 5 grms. respectively, with 4·4 grms. of zirconia, the mixture being heated to bright redness in an iron tube, the mouth of the tube being filled with finely powdered common salt. There remained, after repeated digestion with dilute hydrochloric acid, a fine black powder, so fine that it passed through the filter-paper and remained in part suspended for weeks in water, showing a reddish purple colouration by transmitted light.

When dried and heated in air to a point far below redness it glowed and was transformed into zirconia with a small increase in weight. It evidently consisted of zirconia containing only a small percentage of the metal. When rubbed in an agate mortar, however, it showed no white particles, and the variability of its composition, as shown in these and other experiments, lent no support to the assumption that a lower oxide had been formed. In a second set of experiments, magnesium foil was used, and in this case the foil retained its form, although permeated by metallic zirconium exactly as it does in the reduction of carbon compounds. By separating the foil from the finer powder it was possible to obtain zirconium almost free from oxide. Three specimens were prepared:—A resembled those already described, a velvety black powder, B had a slight greenish cast, and C a decided olive-green colour with a slight lustrous appearance.

It was thought, therefore, that A would prove to be the purest zirconium, judging from the experience of previous experimenters.

Samples were carefully heated in a stream of air, the moisture and carbonic acid (arising from carbon in the magnesium used) directly determined, and the proportion of Zr and ZrO_2 arrived at by calculation, knowing the

* Some of the earlier results had to be rejected because of incomplete washing. 20 grms. of zirconia required to be washed 150 times at the pump before ammonia salts were got rid of, at least 50 litres of water being used in the process.

original weight of substance taken and the weight of ZrO_2 left in the boat.

A simply glowed and passed into a white powder as the previous specimens had done, B burnt with a white light much more brightly than A had done, and C gave out a dazzling light resembling in its brightness that of burning magnesium; when thrown into the flame of a Bunsen burner they gave beautiful white scintillations.

The results of the analysis gave the following composition:—

	A.	B.	C.
Metallic zirconium ..	0·0453	0·1516	0·3383
Zirconia	0·3434	0·3561	0·0267
Moisture	0·0100	0·0086	0·0350
Carbon	0·0015	0·0013	nil

A careful examination showed that no iron or manganese was present, and indeed, after precipitation of the zirconia, the residual impurity from half a grm. weighed less than a m.grm., and consisted entirely of silica, introduced, doubtless, by the ammonia used in precipitation. Preparation C was, therefore, almost pure zirconium, containing only a slight admixture of oxide rubbed up in an agate mortar; it showed a brassy lustre. It is stated generally that zirconium is hardly acted upon at all by mineral acids or aqua regia, but dissolves in hydrofluoric acid. My own observations confirm these statements, with the exception that concentrated sulphuric acid begins to act in the cold even, and on gently warming the action proceeds rapidly with a copious evolution of sulphur dioxide, and even with the production of free sulphur.

Dilute sulphuric acid (1 : 1) acts more slowly with the evolution of hydrogen.

Zirconium is acted upon also by chlorine and bromine, in which, on gentle heating, it undergoes vivid combustion, forming the tetrahaloid derivatives, and this is, indeed, a convenient method for obtaining these bodies. The iodide could not be obtained. When the zirconium was filtered, after the digestion with dilute hydrochloric acid, and dried, it was found to have occluded hydrogen. This was removed by exposing it *in vacuo* for some days, and removing the hydrogen by the mercury pump.

The Oxides.—The only points for remark in addition to what has already been published, relate to the reduction (?) of zirconia and to the peroxide of zirconium.

With regard to the the former it has already been noticed that when zirconia is heated, surrounded by the reducing flame of coal-gas, it blackens. This blackening is only superficial, however, and is in all probability due to a thin deposit of carbon, and it re-oxidises readily to a white powder when heated in air, with a *decrease* of weight—small, indeed, but distinct. Heated at the highest temperature of the blowpipe flame in hydrogen, it undergoes no reduction.

(To be continued).

THE EXPANSION OF THE SPECTRAL RAYS OF THE METALS.

By M. GOUY.

It is known that the spectra of incandescent metallic vapours are formed of rays which, with a small quantity of vapour and with mean dispersion, do not appear to have any sensible breadth. These narrow rays constitute the essential element of gases and vapours at high temperatures, and form almost the totality of the solar spectrum.

If we increase the quantity of the vapour and the power of the spectroscope the strongest of these rays acquire a very appreciable breadth; each of them appears as a small band which remains very continuous, and is not resolved into distinct lines. This is the phenomenon known as the expansion or widening of the spectral rays.

This enlargement is generally effected in an equal manner on both sides of the ray, so that this, when transformed into a small diffused band, appears symmetrical with respect to the position occupied by the fine ray (produced with a small quantity of vapour). This is easily recognised on marking this fine ray with the wire of the grating and increasing the quantity of the vapour employed; the expanded ray is then cut into two equal parts by the wire. The observation is still more distinct in the frequent case where the exterior and refrigerated part of the vapour produces a partial reversion; the extended ray then appears exactly symmetrical with reference to the fine black line which the reversal produces.

This symmetrical structure is important in a theoretical point of view, since certain explanations which might be proposed for the expansion of the rays pre-suppose a perfect symmetry. The author has made some experiments to ascertain if this law is general. The metallic salts were volatilised plentifully in a voltaic arc and were observed by means of a plane grating and a large concave Rowland's grating, which give spectra of an extreme purity.

Almost all the rays observed showed a symmetric enlargement with a perfect distinctness, but certain sodium and potassium rays form a remarkable and most signal exception.

Sodium.—Besides the D rays the vapour of sodium gives a certain number of rays grouped two by two, which have often been regarded as the homologues of the D rays. These rays, in comparison with the D rays, are so much the more intense as the temperature is higher, and they appear reversed in the solar spectrum in the state of fine lines. They have been discovered in very varied conditions, and even in Geissler tubes (Salet), so that they are unanimously attributed to the vapour of metallic sodium.

In the voltaic arc the rays are fine with a very minute proportion of sodium. As this increases they widen, but almost *on one side only*, so that with considerable quantities of vapour they offer the aspect of small bands bounded almost definitely towards the violet side, but fading away on the side towards the red. Their breadth is about half the interval between the rays. Several of them undergo a partial reversal, and then the black line, far from occupying the middle of the band, is very near its right margin (the violet side).

This dissymmetric structure is very marked in the groups 616, 569, 515, 498, 475, 466, and is still visible in two or three fainter groups which terminate this series. The group 567, very feeble, appears, on the contrary, degraded on the side of the violet. But the D rays are enlarged symmetrically. The groups thus mentioned, therefore, present a structure quite different from that of the D rays. Further, in all these groups the least refrangible ray is the strongest, contrary to what exists in the group D. The group 498 is in reality triple, and the groups 569—567 form, rather, a single quadruple group.

Potassium.—The same phenomenon occurs, at least as distinctly, in certain potassium rays. These are the groups 581, 534, 510, 495, 486, and one or two less distinct groups which terminate the series. All these groups are quadruple, and present the closest analogy; each of the component rays is expanded into a band, degraded on the side of the red, but distinctly bounded on the side of the violet, as in the case of sodium. The other red and violet rays of potassium, on the contrary, display a distinctly symmetrical enlargement.

Thus the so-called narrow metallic rays present two distinct structures. Some are expanded in an equal manner on both sides (symmetrical rays), whilst the others broaden almost exclusively on one side (asymmetric rays). The difference is very distinct, and no intermediate case has been observed.

Almost all metallic rays are symmetric, and the only asymmetric rays hitherto observed are those of sodium and potassium, just mentioned.—*Comptes Rendus*, cviii., p. 1236.

ON THE NATURE OF COBALT AND NICKEL.

By Dr. FLEITMANN.

As the author first found in the *Chemiker Zeitung* an account of the surprising communication of HH. Krüss and Schmidt that a new, hitherto unknown, metal was present in nickel and cobalt, he ventures, in the interest of the nickel industry, upon the following remarks. He has repeatedly and carefully examined the most different sorts of nickel and of cobalt oxides of commerce, according to the indications of H. H. Krüss and Schmidt, and even on taking 50 grms. of material he has not been able to obtain ponderable quantities of a substance which would justify the supposition of the presence of a new metal.

The author's experiments were not dictated by an intention to intrude into an investigation which HH. Krüss and Schmidt have reserved for themselves. The interests of the nickel industry, in which he has been concerned for thirty-eight years, made it his duty to decide as quickly as possible so important a fact as the existence of the new metal. After obtaining negative results in his experiments he wrote on Feb. 13th to Dr. Krüss, requesting a small portion of the new metal so as to convince himself of its existence. Dr. Krüss replied on March 29th, promising to forward some preparations. Up to date they have not arrived, and as the writer's continued experiments have proved fruitless, he suspects that "gnomium" exists merely in the imagination of its discoverers. He expects, therefore, from HH. Krüss and Schmidt either a confirmation or a withdrawal of their communications.

According to Dr. Fleitmann's experiments he concludes :—(1). That if cobalt and nickel are regularly accompanied by a hitherto unknown metal this can exist only in extreme traces, and not in quantities up to two per cent. (2). That these traces have no essential influence on the ductility of the nickel, which, in its present state of purity, is as flexible and ductile as the softest iron. (3). That the methods of purifying nickel, patented by Dr. Krüss, are devoid of practical value since they are in part not novel and in part not feasible.

If the nickel and cobalt of trade in the state of hydroxide are treated, as according to Krüss and Schmidt, with excess of sodium hydroxide, we certainly obtain, according to the purity of the materials, varying quantities of the different impurities present in these oxides along with small quantities of nickelous and cobaltous oxides. According to the origin of the sample the impurities consist of small quantities of lead and zinc oxides, arsenic, manganic, molybdic, and silicic acids, alumina, cerium oxides, and chromic acid. The nickelous or cobaltous oxide dissolved does not in general exceed $\frac{1}{20}$ per cent of the oxide used. If it is seperated from the other impurities which exist in solution in the alkaline liquid and converted into nickelous or cobaltous oxide, it is afterwards insoluble in soda-lye, whence its solubility appears to depend on the presence of those impurities, especially arsenic acid, silica, and alumina. If the alkaline extract of the above impurities is mixed with hydrochloric acid until the precipitate formed at first is re-dissolved and ammonium carbonate is then added, there is obtained a wonderful mixture of oxides and acids well calculated to serve as a puzzle. It seems to the author not unlikely that HH. Krüss and Schmidt have met with such mixtures. Their precaution to form the alkaline extract at a low temperature (10°) confirms him in his conjectures, as precipitates often appear on applying heat. Manganic acid and dissolved lead oxide are sometimes converted into manganic oxide and lead peroxide. Still this is merely a conjecture, and he is ready to be convinced to the contrary by more decisive proofs than the discoverers have as yet advanced for the existence of the new element.—*Chemiker Zeitung* (June 12, 1889).

THE ELECTROLYTIC SEPARATION OF CADMIUM FROM ZINC.*

By EDGAR F. SMITH and LEE K. FRANKEL.

THE separation of these metals has been effected by Yoer (*Bull. Soc. Chim. de Paris*, xxxiv., 18), who employed the acetates for this purpose.

Eliasberg (*Zeitschrift für Analyt. Chemie*, xxiv., 548) and Smith and Knerr (*Am. Chem. Journal*, viii., 210) confirmed this observation, at the same time emphasizing the fact that the current should be carefully regulated, otherwise unsatisfactory results would be obtained. A solution containing cadmium and zinc as tartrates, together with free tartaric acid, will also yield all its cadmium to a current generating 0·4—0·5 c.c. oxy-hydrogen gas per minute (*Am. Chem. Journal*, viii., 210). We have no record of other salts of these metals having been used for their electrolytic separation, and therefore have taken occasion to learn what might be the result with solutions of the double cyanides, such as we employed in separating mercury and copper (*Journal Franklin Institute*, cxxvii., 386, and *Am. Chem. Journal*, xi., 264).

Beilstein and Jawein (*Ber. d. Deutsch. chem. Gesellschaft*, xii., 446, 762) have shown that both cadmium and zinc can be completely precipitated from a cyanide solution, but have not given the current strength employed by them in their experiments, nor did they attempt the separation of these metals from each other.

As our experience with mercury and copper clearly indicates, it is frequently possible, by close attention to the current, to effect electrolytic separations, which ordinarily seem impossible. With this fact clearly before us, our first work with the metals now under consideration was to ascertatain how feeble a current would suffice for the complete deposition of each metal, when alone in a cyanide solution, in the presence of an excess of an alkaline cyanide. We very soon discovered that the cadmium separated readily and with a much weaker current than was necessary for the deposition of the zinc. The latter will, however, separate from a cyanide solution, even under the influence of a feeble current, but not until the excess of cyanide has been completely decomposed. With the quantity of cyanide used by us, and with a current of the strength indicated below, this complete decomposition of the alkaline cyanide is not likely to occur in a shorter period than forty-eight hours. Hence it follows that, as the quantity of cadmium used in our experiments is

Metallic Cadmium in Grms.	Cadmium found.	Metallic Zinc present.	Difference in p.c. of Cadmium.	KCN in grms.	Total Dilution.	Current in c.c. of OH Gas.	Time.
			Per cent.				
0·1817	0·1813	—	−0·22	4·5 grms. in each separation.	200 c.c.	0·3 c.c. in each experiment.	18-23 hours.
	0·1818	—	+0·05				
	0·1815	—	−0·11				
	0·1822	—	+0·22				
	0·1812	0·2000	−0·27				
	0·1818	0·2000	+0·05				
	0·1828	0·2000	+0·60				
0·2426	0·2422	—	−0·16				
	0·2432	—	+0·24				
	0·2426	—	—				
	0·2420	0·2000	−0·24				
	0·2435	0·2000	+0·30				
	0·2429	0·2000	+0·12				
	0·2426	0·2000	—				
	0·2433	0·2000	+0·28				
	0·2434	0·2000	+0·32				

* Read at the Meeting of the Chemical Section of the Franklin Institute, May 21, 1889.

entirely precipitated in a little more than eighteen hours, the complete separation of cadmium from zinc is thoroughly feasible by this method.

All our experiments were conducted in the cold, and care was taken in each case to examine the deposited metal for zinc and the residual solution for cadmium. The conditions under which our work was carried on and the results obtained are given in the Table.

The cadmium deposit was light grey in colour and crystalline in structure. It was washed with hot water and dried upon a warm iron plate.

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

June 22, 1889.

Prof. REINOLD, F.R.S., President, in the chair.

MAJOR P. CARDEW, R.E., and Mr. A. W. Ward, M.A., were elected Members.

The following communications were made :—

"*Note on Some Photographs of Lightning and of Black Electric Sparks.*" By Mr. A. W. CLAYDEN.

The lightning photographs, three in number, were obtained during the storm on the 6th inst. Two flashes seen on one plate show a complicated and beautiful structure. One of them is a multiple flash, and flame-like appendages point upwards from every angle. The other is a broad ribbon, and although the plate shows signs of movement, the displacement is not in a direction such as would produce a ribbon-like effect from a simple flash. The second plate shows four flashes, none of which are ribbon-like, though the camera had moved considerably. The third plate was exposed to six flashes, one of which was believed to pass down the middle of the plate, but, on development, only a triple flash in one corner of the plate was seen. Careful search, however, revealed the central flash as a dark one with a white core, and other dark flashes were subsequently found. The plate was very much over-exposed, and this suggested that black flashes might be due to a sort of cumulative action, caused by the superposition of the glare from a white cloud upon the normal image of the flash. To test this, sparks from a Wimshurst machine were photographed, and, before development, the plates were exposed to diffused gaslight for a short time. The bright sparks yielded normal images with reversed margins, and the faint ones were completely reversed. Other experiments showed the reversal to spread inwards as the time of exposure to gaslight increased. Finally, reversal was effected by placing a white screen behind the spark to represent a white cloud, the only illumination being that of the spark itself.

In the discussion which followed Mr. W. N. SHAW exhibited a photograph taken during the same storm, which is particularly rich in dark flashes branching outwards from an intensely bright one. In some places the bright line has dark edges, and in one part a thin bright line runs along the middle of an otherwise dark portion of the flash.

In answer to Mr. Inwards, Mr. Shaw said the plate was exposed about half a minute, and the former thought that under those conditions the appearance of the plate did not contradict Mr. Clayden's hypothesis.

Speaking of the same photograph, Prof. PERRY considered that Mr. Clayden's observations would explain the result, for a bright flash required more exposure to diffused light to reverse it than a faint one did.

Prof. RAMSAY reminded the meeting that Prof. Stokes's "oxides of nitrogen" explanation of dark flashes was still a possible one, and Mr. C. V. BURTON asked whether they may be due to faint sparks cutting off light from brightly illuminated clouds, just as a gas-flame absorbs light from a brighter source.

In reply, Mr. CLAYDEN thought the "oxides of nitrogen" hypothesis improbable, and said his experiments did not enable him to answer Mr. Burton's question. As regards Mr. Shaw's plate, he believed the diffused light from the clouds would be sufficient to reverse the fainter tributary flashes, although it was insufficient to reverse the primary one.

From data obtained when the ribbon flash was taken he had made some calculations which gave the height of the clouds about 1000 yards, and the ribbon flash 1300 yards long and 100 yards wide.

"*Researches on the Electrical Resistance of Bismuth.*" By Dr. ED. VON AUBEL.

The paper, which is in French, was taken as read. A translation will appear in the *Proceedings* of the Society.

"*Expansion with Rise of Temperature of Wires under Pulling Stress.*" By J. T. BOTTOMLEY, M.A., F.R.S.

The investigation was to determine whether the coefficient of expansion of wires depends on the stress to which they are subjected, and was undertaken in connection with the secular experiments on the elasticity and ductility of wires, now being conducted at Glasgow University.

Two wires, about 17 ft. long, of the same material, were suspended side by side within a tube through which steam could be passed to change the temperature. One wire was loaded to half, and the other to one-tenth its breaking weight, and in the preliminary experiments the elongations were read by a Quincke's microscope cathetometer. About 150 heatings and coolings, extending over three months, were necessary to bring the heavily loaded wire to its permanent state, so that consecutive expansions and contractions were equal. When this stage was arrived at, hooks of peculiar shape were attached to the lower ends of the wire. These hooks form a relative geometrical guide, and their horizontal parts mutually support a small table which carries a plane mirror. If the wires expand or contract unequally the mirror becomes tilted, and the relative displacement is observed by means of a telescope and scale fixed nearly vertically over the mirror.

From experiments on copper wires the coefficient of relative expansion was found to be $0{\cdot}32 \times 10^{-6}$ per degree Centigrade, or about $\frac{1}{5}\frac{1}{5}$th of the ordinary linear expansion of the material. The heavily loaded wire expanded most. The results for platinoid give $0{\cdot}27 \times 10^{-6}$ as the relative coefficient under the conditions named above; this is about $\frac{1}{3}\frac{1}{7}$th of the ordinary linear expansion, which, from separate experiments, was found to be $15{\cdot}4 \times 10^{-6}$.

Mr. H. TOMLINSON thought the probationary period for copper might be considerably shortened by repeatedly putting on and taking off the load, and by subjecting the wire to torsional oscillation. With iron wires this would not be the case, for they behave in a most peculiar manner, and require long periods of rest after each oscillation. From experiments he had conducted during the last two years he found that the permeability of iron could be enormously reduced by repeated heatings and coolings, whilst undergoing magnetic cycles of small range.

Mr. GREGORY said the paper threw considerable light on some experiments on the sag of stretched wires, upon which he was engaged. He also suggested heating the wires by electric currents.

In reply, Mr. BOTTOMLEY said he had considered it important to leave the wires untouched after being suspended, and, as regards heating by electricity, he thought that convection currents would make the temperature non-uniform.

Owing to the absence of Prof. S. P. Thompson his "Notes on Geometrical Optics" were postponed.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, July 1, 1889.

Mr. WILLIAM CROOKES, F.R.S., Vice-President, in the Chair.

THE following were elected Members of the Royal Institution :—Robert Kaye Gray ; James Mactear, F.R.S.E., F.C.S. ; William James Russell, PhD., F.R.S., Pres.C.S. ; and James Miln Small.

Sir James Crichton Browne, M.D., LL.D., F.R.S., was elected Treasurer of the Royal Institution in the room of Henry Pollock, deceased.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

OBITUARY.

DR. JOHN PERCY.

THE eminent chemist and metallurgist, Dr. John Percy, came to the end of his meritorious career on Wednesday, June 19. The deceased was born at Nottingham in 1817, and, selecting the medical profession, he entered the University of Edinburgh, where he graduated as M.D. at the age of 21. He was at the same time the pupil of Sir Charles Bell and the fellow-student of E. Forbes. After graduation he continued his medical studies at Paris. Returning from France, after making a botanical tour in the Pyrenees, he became physician to the Queen's Hospital at Birmingham. Whilst residing in that town his attention was drawn to the chemistry of metallurgy, and to such good purpose that when, in 1851, the Government School of Mines was organised, he was appointed to the Chair of Metallurgy at the recommendation of De la Beche. This position Dr. Percy held for twenty-eight years, and it is not too much to say that he contributed in an eminent degree to the success of this Institution. When, in 1879, the School of Mines was absorbed by the Science and Art Department, Dr. Percy resigned his professorship.

His *magnum opus* is an exhaustive treatise on metallurgy, the first volume of which appeared in 1861. In 1864 followed the second part, dealing with iron and steel, and this was followed subsequently by other volumes discussing lead, silver, and gold.

Dr. Percy, until his death, was superintendent of the ventilation arrangements in the Houses of Parliament.

NOTICES OF BOOKS.

Chemistry, General, Medical, and Pharmaceutical, Including the Chemistry of the British Pharmacopœia. A Manual of the General Principles of the Science and their Applications in Medicine and Pharmacy. By JOHN ATTFIELD, F.R.S. Thirteenth Edition. London: Gurney and Jackson.

WHEN a book has passed through the ordeal of thirteen editions in the lapse of twenty-two years its standing must be viewed as fully established, and much of the ordinary work of the reviewer is found to be needless. We may, however, remark on the very judicious manner in which the author, in his preface, explains the character and aim of his work. He fully recognises that the principles of chemistry are the same for all students to whatever purpose they may ultimately be applied. But these same principles may be expounded and illustrated in very varied manners according to such ultimate purpose. Thus chemistry may be legitimately taught differently to the metallurgist, to the agriculturist, to the tinctorialist, and to the pharmacist. It will not be thought a digression if we point out that the time is not far distant when the pharmacist will require a much more profound knowledge of chemistry than it has hitherto been deemed necessary. It may even some day be found possible to ascertain the physiological action of any novel compound—natural or synthetic—by a study of its chemical constitution. We hope that both the teachers and the students of pharmacy will keep this view in mind as a goal to be aimed at.

We are much pleased with the author's "Advice to Students Respecting their Object in Studying." He has no unqualified sympathy with examinationism and with the common plan of studying to prepare for and pass this or the other examination. He considers, however, that it is "the least unsatisfactory (test) that has been devised." Has earnest and continuous effort been applied to devising a better? In the meantime we submit that in many cases the production of original work is a much more satisfactory test of mental discipline than the power of passing examinations. But we are not prepared to argue that this method would be available in pharmaceutical study.

A passage quoted from Lord Lytton and placed as a motto at the back of the title-page calls for a word of comment. Says Lord Lytton :—"I hold that the greatest friend to man is labour." If by "labour" he means the systematic employment of brain and muscle to some definite end, he is right. But if he uses "labour" in the technical sense of political economists, as work which is "susceptible of pecuniary compensation or material advantage," he is signally wrong. The highest work in science—the life-work of such men as Darwin—cannot be economically appraised. Prof. Fiske says that the man of original scientific or philosophical genius "should never be called upon to earn a living; for that is a wretched waste of energy, in which the highest intellectual power is sure to suffer serious detriment, and runs the risk of being frittered away into hopeless ruin."

Dr. Attfield's work is fully worthy of the reputation which it has acquired, and is not likely, for the present, to be superseded.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 23, June 11, 1889.

Solubility of Saccharose in Distilled Water.—Léon Périer.—At a given temperature and a total volume of 100 c.c. of liquid each grm. between 1 and 45 per cent increases the densimetric expression of the solution by a constant value ; from 45 to 90 per cent (the maximum of solubility in the cold) the increase is less regular.

On the Rectification of Alcohol.—E. Sorel.—A mathematical paper, not admitting of useful abstraction.

Bulletin de la Société Chimique de Paris. Vol. i., (Ser. 3), No. 10. May 20, 1889.

Determination of Mono-methyl-aniline.—The authors weigh into a small flask (capable of being set on a water-bath and connected with an ascending condenser) from 1 to 2 grms. of the mixture to be analysed. They introduce into the mixture as rapidly as possible a known weight of acetic anhydride corresponding to about double the weight of the mixture. The flask is connected to the condenser and the reaction is then allowed to proceed for half-an-hour at the temperature of the atmosphere. About 50 c.c. of water are then introduced and the flask is then

heated for forty-five minutes on the water-bath. The flask is then cooled, the liquid made up to a known volume, and the acetic acid present is titrated by means of a standard solution of soda, using phenolphthalein as indicator. They then calculate to what quantity of monomethyl-aniline the acetic acid consumed must correspond, having of course deducted the quantity necessary for acetyling the aniline in the mixture.

Preparation and Purification of Amyl Iodide.—H. Malbot.—The author operates upon 240 c.c. of amylic alcohol, 20 grms. red phosphorus, and 200 grms. iodine. He eliminates the alcohol by means of very strong hydrochloric acid.

The Manganese Oxides obtained in the Moist Way.—Alex. Gorgen.—Hydrated manganous acid, in contact with an excess of precipitated manganous oxide, produces saturated manganite, $MnO_2 2MnO$. In presence of an excess of manganous carbonate it yields only an acid manganite, and in neutral solutions kept in that state manganous acid absorbs merely the quantity of manganous oxide corresponding to one of the acid manganites.

Action of Air on Manganese Carbonate. Can this Reaction give Rise to any of the Natural Peroxides?—A. Gorgen.—Not suitable for useful abstraction.

Zeitschrift fur Physikalische Chemie.
Vol. iii., Part 1.

The Origin of the Current in a Galvanic Combination.—L. Sohncke.—The author considers that the conception of fluidity founded by Clausius with the mere addition of a fundamental chemical fact seems capable of rendering readily intelligible the mechanism of the origin of a current in a galvanic circuit. The view of Clausius includes two hypotheses; that of contact and that of dissociation. The fundamental chemical fact is that different substances exert upon one and the same body chemical attractions of different strength.

The Conditions of Equilibrium between Chlorine and Iodine.—W. Stortenbeker.—This paper requires the accompanying illustrations.

The Action of Ferments.—G. Tammann.

On Raoult's Law of Congelation.—R. Fabinya.—Both these papers require the accompanying figures and tables.

MISCELLANEOUS.

Improved Balance.—At the Hamburg Exhibition of Trades and Industries Max Beckel displays an analytical balance, the sensitiveness of which can be modified at pleasure.—*Chemiker Zeitung.*

Sewage Treatment at Kingston-on-Thames.—On Saturday, June 29th, the works for the treatment of the sewage of Kingston and Surbition were formally inaugurated in presence of a numerous gathering of municipal authorities, medical practitioners, chemists, engineers, and others interested in sanitary questions. The process adopted is that form of the absorption-precipitation system known as the "A B C," and is conducted by the Native Guano Company, Limited. The offensive matters are first absorbed or occluded by the addition of finely ground clay and carbon, and the whole is then treated with a salt of aluminium. The mixture is then allowed to subside in a series of tanks; whence the effluent water passes out to the Thames, clear, inodorous, and having that faintly blue tint which marks the removal of dissolved organic impurities. So complete was the deodorisation that, though the day was hot and almost calm, the visitors, when sitting down to lunch in a marquée on the leeward side of the works, tanks, &c., could perceive no offensive smell. The works, as at present constructed, meet the requirements of 38,000 people, and we are told that with some comparatively trifling additions they can be arranged for a population of 50,000.

Determination of Phosphoric Acid in Superphosphate.—Julius Stoklasa.—10 grms. of the sample are placed in one litre of water. Of the filtrate 50 c.c. are mixed with a solution of ammonium citrate and magnesia mixture, and well shaken for five to six minutes in a shaking apparatus. Ammonia is then added to the extent of one-fourth of the entire volume of liquid. The magnesium ammonium phosphate is then filtered in a perforated platinum crucible; in this it is washed, ignited, and weighed as pyrophosphate. The ammonium citrate solution is obtained by dissolving 250 grms. citric acid in ½ litre of water and using 20 c.c. of this solution, after being neutralised with ammonia.—*Chemiker Zeitung* (*Coethen*).

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Thiocamf.—I should be much obliged if any of your correspondents could let me know where I could purchase the new disinfectant, thiocamf, described on p. 291, vol. lix., Chemical News, June 21, 1889.—G. E. Wright.

Prof. A. E. FOOTE,
of Philadelphia, Pa.,
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THE CHEMICAL NEWS.

Vol. LX. No. 1546.

THE CONDITIONS OF ACTION OF NITRIC ACID.

By C. F. CROSS and E. J. BEVAN.

The appearance of a paper by Mr. V. H. Veley on this subject, or rather upon one aspect of it, affords a convenient opportunity of recording some experimental results which have accumulated during the last year or two, bearing upon this question of the exact mechanism of the actions of nitric acid. The directions of investigation have been various, and we briefly record the main results under their respective heads.

Action of Dilute Nitric Acid upon Ligno-celluloses with and without Addition of Urea.—Our observation that the presence of urea arrests the specific action of nitric acid upon the lignified celluloses, changing it into one of simple hydrolysis, as in the case of the stable mineral acids, is recorded in "Watts's Dic.," New Ed., Art. "Cellulose." We take from our note-book (1887) the following record of experiments :—

(*a*). Four portions of jute fibre of 2 grms. each; with 50 c.c. of nitric acid of 1·05 sp. gr.; weights of urea added, 0·1, 0·2, 0·3, 0·4 respectively; digested seven hours at 60° to 70°. The fibrous residues were then washed, dried, and weighed. The results are given as percentage yield, with the external characteristics of the products :—

(1).	68·0	per cent.	Pale yellow, approximating to cellulose.
(2).	71·1	,,	Brownish yellow.
(3).	75·4	,,	Reddish yellow.
(4).	77·2	,,	Mahogany red, differing but little from the original.

With the graduated increase of urea there is a gradual departure from the characteristic action of the pure acid, which we have investigated and described on previous occasions, and in regard also to the soluble products of the reaction in which corresponding variations between the two extremes were observed. To complete the above series we may mention that under these conditions of digestion of the fibre with the pure dilute acid the reduction to cellulose is complete, the yield amounting to 60—65 per cent. It is scarcely necessary to say that by largely increasing the urea—added in the form of nitrate—beyond the maximum proportion above given an even greater divergence may be determined, and as the results are very evident to the senses, the comparison makes a striking lecture demonstration.

These results led us to extend the investigation of the influence of urea—*i.e*, of the elimination of nitrous acid—to other actions of nitric acid. We exposed metallic copper—as Mr. Veley has done—in the form of a wire spiral ($\frac{1}{16}$ in.) of the pure metal, to acid of 1·05 sp. gr. at 60°, with and without the addition of urea, the quantity of acid being 50 c.c., and of copper 4·465 in two comparative experiments. In the case of the pure dilute acid a digestion of four hours was required for the complete dissolution of the metal. With the addition of 1 grm. urea, the weight lost at the expiration of three hours was only 0·020 grm. Further, similar experiments afforded us sufficient evidence of what Mr. Veley has now proved by means of his carefully elaborated method, viz., that the interaction of nitric acid and the metals is another instance of dependence upon the *tertium quid*, which in this case could scarcely be other than nitrous acid.

Action of "Nitrating" Mixture ($HNO_3+H_2SO_4$) *with and without Addition of Urea.*—It appeared that the investigation of this point might throw further light upon the formation and constitution of the explosive derivatives obtained from the celluloses and compound celluloses. We made a series of comparative "nitrations," both of cotton and the jute fibre, with and without addition of urea to the acid mixture. The evidence as to its influence on the reaction was uniformly negative, a result which strengthens the evidence that the derivatives in question are alcoholic nitrates. When, on the other hand, the formation of a nitro-derivative is involved, the presence of urea may have a very important influence, as indeed Dr. Perkin, Jun., showed in a recent note communicated to the Chemical Society on the "Nitration of Anthracene in Presence of Urea," this modification of the conditions being proved to determine a simple substitution in the carbon nucleus.

The last point to which we desire to call attention is a decomposition which would appear to stand in direct contrast to those already discussed, although, like these in illustrating the dependence of reactions upon an intermediary third substance; the reaction in question is the *complete combustion of urea by chromic acid, in presence of nitric acid.* In the course of working out the method of ultimate analysis of carbon compounds by combustion with chromic anhydride in presence of sulphuric acid (*Chem. Soc. J.*, 1888, 889), we observed that the decomposition of nitrogen compounds was generally very incomplete. Recalling the fact that urea survives the very severe combustions of the animal body, we made experiments upon this compound and found in effect that it entirely resisted the action of the chromic mixture. On one occasion we happened to employ a silver chromate prepared by precipitation from the nitrate, and were surprised to find that a rapid combustion ensued, resulting in the complete conversion of the urea into gaseous products (CO_2+N_2). Investigation of this particular specimen of chromate showed it to contain a small quantity of residual nitric acid. That this was the determining agent in the decomposition was shown by direct experiments, of which the following are the details :—

(1). Urea taken, 0·1509; 9 c.c. H_2SO_4 with excess of CrO_3 (1—2 grms.) and 0·500 grm. KNO_3.
Vol. of gas collected, 121 c.c. at 20° and 756 m.m.
Corrected vol., 112·7 c.c.
Deducting vol. of nitrogen, calc.—

$$\frac{0{\cdot}0703}{1{\cdot}256} \times 1000 = 56 \text{ c.c.}$$

leaves 56·7 c.c. CO_2, from which carbon percentage of urea = 20·1 (calc., 20·0).

(2). 0·1502 urea. Conditions as in (1).
Vol. of gas collected, 121·5 c.c. at 19° and 755 m.m.
Corrected vol., 113·0. Taking one-half as CO_2 and calculating the carbon percentage we obtain 20·2.

(3). 0·1522 urea. Conditions as in (1).
Vol. of gas collected, 125·0 c.c. at 20° and 752 m.m.
Carbon percentage calc. from corr. vol. $= \frac{115{\cdot}2}{2} = 20{\cdot}2$.

These numbers are higher than those obtained in the combustion of nitrogen-free compounds by this method, the slight absorption of the gaseous products by the sulphuric acid appearing to be exactly balanced by the tension of the nitric acid added. Similarly, in regard to this latter point, we found that picric acid, which yielded at once to the acid mixture, the combustion completing itself rapidly, yielded a volume of CO_2, from which the percentage number calculated was identical with the theoretical. In this case it was of course unnecessary to add nitric acid. Aniline, which we had been unable to burn satisfactorily with the chromic mixture, underwent complete combustion in presence of nitric acid, added as in the above experiments. The numbers obtained (percentage) were constant, and again slightly in excess of

the theoretical. In this case no nitrogen was evolved, being entirely retained by the acid as ammonia.

Reverting now to the question of the equilibrium of the urea molecule, we find that under the conditions of this combustion it is stable, but that the introduction of nitric acid suffices to upset it. Its influence in determing the rupture of the molecule would appear to be specific, for we found that vanadium pentoxide, which from all analogies might be expected to behave similarly, was entirely without influence. To explain the specific action of the nitric acid, according to the generally received view, we must assume reduction to the lower state of oxidation and contact in this form with the amide nitrogen, with the usual result: $2NH_3+N_2O_3=3H_2O+2N_2$. It is difficult, however, to see how this can take place, even locally, under such powerful oxidising conditions. Anticipatory explanations have, moreover, little value outside a text-book; if adopted in the laboratory they rather obstruct hy making appear unnecessary the prosecution of the search for the actual cause up to the limits of the experimental method. We confess our inability to offer an adequate explanation: but the fact is for the present more important. We shall continue our investigation of these points as opportunity offers, but without wishing to make any reservation to ourselves in so wide a field of research on account of priority. Mr. Veley having announced his intention of extending his researches to other metals, using the methods described, we willingly relinquish this portion of the subject with a due acknowledgment of the perfection of detail of his methods. But in regard to the general study of the conditions of action of nitric acid, we shonld expect that most chemists engaged in research could contribute some observations which, if gathered together from all sources, would make an imposing and interesting chapter in chemical mechanics.

4, New Court, Lincoln's Inn,
June 28, 1889.

THE ANALYSIS OF GLASSES.

By DAVID LINDO.

We have learnt with deep regret of the demise of our highly valued contributor, Mr. David Lindo, of Falmouth, Jamaica. He died on May 7th after a painful illness of six weeks, during which he had to undergo the operation of lithotomy. His executor has kindly forwarded to us the notes of an incomplete investigation on the analysis of glass which our late correspondent had taken up a few months prior to his end. His attention had been drawn to this subject as he had found most of his beakers, test-tubes, &c., became cloudy within. On testing them with phenolphthalein he found that not merely the cloudy glasses, but those also which were to all appearance perfectly clear and bright, turned a rich magenta colour when the test was applied.

For the determination of silica in the several samples 2 grms. of the glass in very fine powder were taken. The author took first something over 2 grms. in small fragments, which, after weighing, were crushed in the steel mortar, ground fine in a large agate mortar, transferred to a platinum crucible, ignited gently, placed in the desiccator, carried to the balance while warm, and two grms. exact were quickly weighed out. The glass was then fused in a large platinum crucible with 8 grms. of alkaline mixture (13 parts potassium carbonate and 10 parts sodium carbonate), heating first gently, then more strongly for half an hour more with large concentric spirit-lamp, and then for a quarter of an hour with blast-lamp urged with multiple blowpipe; the crucible was cooled generally in water after spreading the fusion over the surface, some distilled water added to contents, and heated some time on sand-bath, which treatment nearly dissolved out the contents, which were then transferred to a beaker. More water was then added to the residue in the crucible and heated cautiously hy means of a spirit-lamp, moving the latter about under the crucible and not allowing the contents to boil. In this way the residue was easily dissolved out, transferred to the beaker, and rinsed well; finally, with the HCl to be used for decomposition, he rinsed the cover of the crucible in the acid, and covered the beaker with a clock-glass. He then added the acid cautiously (30 c.c. HCl, diluted with the washings of the crucible). After heating for some time on the sand-bath the whole was transferred generally the next day to a large platinum dish, evaporated to dryness, reduced to powder with an agate pestle, and heated ahout two hours longer on the sand-bath. It was then moistened with 6 or 8 c.c. HCl and a little water, let rest for several hours, though it is not absolutely necessary to wait so long. There were then added 60 c.c. of water, the whole was heated and filtered into a 200 c.c. flask, washed well with hot water, the washings concentrated and added to the contents of the flask. The silica was dried in the stove, placed in a platinum crucible, the filter was burnt, and its ash put into the crucible and mixed with 6 or 7 grms. alkaline mixture. The whole was then fused again as above, and dissolved out again as before; the solution was always brilliantly clear. To get the silica in a vitreous form it was sufficiently diluted with water before adding the 25 c.c. HCl. In one or two instances the silica was partly precipitated, the dilution not being sufficient. He proceeded as with the first or crude silica, except that the quantity of water was 50 c.c. instead of 60 c.c., and the silica was collected in a Gooch crucible, and the filtrate and concentrated washings were added to the contents of the flask. 200 c.c. of hot water are quite sufficient to wash this silica provided it is all in the vitreous form, as it is then washed much more easily than when it is in the ordinary amorphous condition. Hence it is always better to obtain silica in the vitreous state. The greater dilution which this requires renders the evaporation more tedious, but this is more than compensated by the more rapid and satisfactory washing. The silica is always beautifully white. A little, of course, passes into solution, as the ammonia precipitates are often insufficient to carry this dissolved silica down. The author therefore prepared some ferric chloride containing a slight excess of HCl, and precipitated 10 c.c. in the flask with ammonia in slight excess. He then filtered through a Gooch, washed well with hot water, ignited, and weighed. By this means the last trace of silica was recovered from the solutions. The silica will therefore generally be separated—(1). From the whole mass of salts (which may be called the bulk). (2). From the ammonia precipitates. (3). From the filtrate given by ammonia, carrying down the last trace with ferric oxide. The bulk was ignited first with the spirit-lamp, and then heated for eight minutes with the flask. On this there was no further loss. The small residues were ignited with the larger spirit-lamp, using the mouth blow-pipe.

No. 28. In a 300 c.c. cloudy flask the percentage of silica found was 73·13.

No. 10. Some test-tubes *not* cloudy yielded 68·94 per cent silica.

No. 3. In other test-tubes which were turning cloudy, and which when pulverised appeared deeply blue from the presence of manganese, the silica was 70·61 per cent.

No. 22. A cloudy pint tumbler (moulded) yielded a bluish green mass, not very dark, and contained 73·06 per cent of silica.

No. 29. A 300 septem flask, *not* cloudy, giving a mass coloured deeply blue with manganese, contained 71·49 per cent silica.

No. 34A. French glass tubing, *not* cloudy, giving a deep blue mass, yielded 69·86 per cent of silica.

No. 34B. French glass tubing, not cloudy (part of same tube as the foregoing), contained 70·11 per cent of silica.

No. 8. Pipette, cloudy mass, blue with manganese, gave 67·23 per cent of silica.

No. 1. Clear flask, reacting strongly with phenolphthalein and forming a blue mass (manganese), showed 72·42 per cent of silica.

No. 5A. 100 c.c. flask, turned cloudy, mass white, containing no manganese. The silica was 72·96 per cent.

No. 31. Clear retort glass, reacting slightly with phenolphthalein, and yielding a deep blue mass with a violet reflection. Silica, 73·70 per cent.

(To be continued).

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY.*

By D. MENDELEEFF, LL.D.,
Professor of Chemistry in the University of St. Petersburg.

(Continued from p. 4).

But while speaking of the application of the principle of substitution to water, we need not multiply instances, but must turn our attention to two special circumstances which are closely connected with the very mechanism of substitutions.

In the first place, the replacement of two atoms of hydrogen by one atom of oxygen may take place in two ways, because the hydrogen molecule is composed of two atoms, and therefore, under the influence of oxygen, the molecule forming water may separate before the oxygen has time to take its place. It is for this reason that we find, during the conversion of alcohol into acetic acid, that there is an interval during which is formed aldehyd, C_2H_4O, which, as its very name implies, is "alcohol dehydrogenatum," or alcohol deprived of hydrogen. Hence aldehyd combined with hydrogen yields alcohol; and united to oxygen acetic acid.

For the same reason there should be, and there actually are, intermediate products between ammonia and nitric acid, $NO_2(HO)$, containing either less hydrogen than ammonia, less oxygen than nitric acid, or less water than caustic ammonia. Accordingly we find, among the products of the de-oxidisation of nitric acid and the oxidisation of ammonia, not only hydroxylamine, but also nitrous oxide, nitrous and nitric anhydrides. Thus, the production of nitrous acid results from the removal of two atoms of hydrogen from caustic ammonia and the substitution of the oxygen for the hydrogen, $NO(OH)$; or by the substitution, in ammonia, of three atoms of hydrogen by hydroxyl, $N(OH)_3$, and by the removal of water; $N(OH)_3 - H_2O = NO(OH)$. The peculiarities and properties of nitrous acid, as, for instance, its action on ammonia and its conversion, by oxidation, into nitric acid, are thus clearly revealed.

On the other hand, in speaking of the principle of substitution as applied to water, it is necessary to observe that hydrogen and hydroxyl, H and OH, are not only competent to unite, but also to form combinations with themselves, and thus become H_2 and H_2O_2; and such are hydrogen and the peroxide thereof. In general, if a molecule AB exists, then molecule AA and BB can exist also. A direct reaction of this kind does not, however, take place in water; therefore undoubtedly, at the moment of formation hydrogen reacts on the peroxide of hydrogen, as we can show, at once, by experiment; and, further, because the peroxide of hydrogen, H_2O_2, exhibits a structure containing a molecule of hydrogen, H_2, and one of oxygen, O_2, either of which is capable of separate existence. The fact, however, may now be taken as thoroughly established, that, at the moment of combustion of hydrogen or of the hydrogen compounds, peroxide of hydrogen is always formed, and not only so, but in all probability its formation invariably precedes the formation of water. This was to be expected as a consequence of the law of Avogadro and Gerhardt, which leads us to expect this sequence in the case of equal interactions of volumes of vapours and gases; and in the peroxide of hydrogen we actually have such equal volumes of the elementary gases.

The instability of peroxide of hydrogen—that is to say, the ease with which it decomposes into water and oxygen, even at the mere contact of porous bodies—accounts for the circumstance that it does not form a permanent product of combustion, and is not produced during the decomposition of water. I may mention this additional consideration that, with respect to the peroxide of hydrogen, we may look for its effecting still further substitutions of hydrogen by means of which we may expect to obtain still more highly oxidised water-compounds, such as H_2O_3 and H_2O_4. These Schönbein and Bunsen have long been seeking, and Berthelot is investigating them at this moment. It is probable, however, that the reaction will stop at the last compound, because we find that, in a number of cases, the addition of 4 atoms of oxygen seems to form a limit. Thus, OsO_4, $KClO_4$, $KMnO_4$, K_2SO_4, Na_3PO_4, and such like, represent the highest grades of oxidation.*

As for the last forty years, from the time of Berzelius, Dumas, Liebig, Gerhardt, Williamson, Frankland, Kolbe, Kekulé, and Butlerow, most theoretical generalisations have centered round organic or carbon compounds, so we will, for the sake of brevity, leave out the discussion of ammonia-derivatives, notwithstanding their simplicity in respect to the doctrine of substitutions; we will dwell more especially on its application to carbon compounds, starting from methane, CH_4, as the simplest of the hydrocarbons, containing in its molecule one atom of carbon. According to the principles enumerated we may derive from CH_4 every combination of the form CH_3X, CH_2X_2, CHX_3, and CX_4, in which X is an element, or radical, equivalent to hydrogen, that is to say, competent to take its place or to combine with it. Such are the chlorine substitutes mentioned already, such is wood-spirit, $CH_3(OH)$, in which X is represented by the residue of water, and such are numerous other carbon derivatives. If we continue, with the aid of hydroxyl, further substitutions of the hydrogen of methane, we shall obtain successively $CH_2(OH)_2$, $CH(OH)_3$, and $C(OH)_4$. But if, in proceeding thus, we bear in mind that $CH_2(OH)_2$ contains two hydroxyls in the same form as peroxide of hydrogen, H_2O_2 or $(OH)_2$, contains them—and moreover, not only in one molecule, but together, attached to one and the same atom of carbon—so here we must look for the same decomposition as that which we find in peroxide of hydrogen, and accompanied also by the formation of water as an independently existing molecule; therefore $CH_2(OH)_2$ should yield, as it actually does, immediately water and the oxide of methylene, CH_2O, which is methane with oxygen substituted for two atoms of hydrogen. Exactly in the same manner out of $CH(OH)_3$

* A Lecture delivered at the Royal Institution of Great Britain, May 31, 1889.

* Because more than four atoms of hydrogen never unite with one atom of the elements, and because the hydrogen compounds (*e.g.*, HCl, H_2S, H_3P, H_4Si) always form their highest oxides with four atoms of oxygen, and as the highest forms of oxides OSO_4, RO_4 also contain four of oxygen, and eight groups of the periodic system, corresponding to the highest basic oxides R_2O, RO, R_2O_3, RO_2, R_2O_5, RO_3, R_2O_7, and RO_4, imply the above relationship, and because of the nearest analogues among the elements—such as Mg, Zn, Cd, and Hg: or Cr, Mo, W, and U; or Si, Ge, Sn, and Pt; or F, Cl, Br, and J, and so forth—not more than four are known, it seems to me that in these relationships there lies a deep interest and meaning with regard to chemical mechanics. But because, to my imagination, the idea of unity of design in Nature, either acting in complex celestial systems or among chemical molecules, is very attractive, especially because the atomic teaching at once acquires its true meaning, I will recall the following facts relating to the solar system. There are eight major planets, of which the four inner ones are not only separated from the four outer by asteroids, but differ from them in many respects, as, for example, in the smallness of their diameters and their greater density. Saturn with his ring has eight satellites, Jupiter and Uranus have each four. It is evident that in the solar systems also we meet with these higher numbers four and eight which appear in the combination of chemical molecules.

are formed water and formic acid, CHO(OH), and out of $C(OH)_4$ is produced water and carbonic acid, or directly carbonic anhydride, CO_2, which will therefore be nothing else than methane with the double replacement of pairs of hydrogen by oxygen. As nothing leads to the supposition that the four atoms of hydrogen in methane differ one from the other, so it does not matter by what means we obtain any one of the combinations indicated —they will be identical; that is to say, there will be no case of actual isomerism, although there may easily be such cases of isomerism as have been distinguished by the term metamerism.

Formic acid, for example, has two atoms of hydrogen, one attached to the carbon left from the methane, and the other attached to the oxygen which has entered in the form of hydroxyl, and if one of them be replaced by some substance X it is evident that we shall obtain bodies of the same composition, but of different construction, or of different orders of movement among the molecules, and therefore endowed with other properties and reactions. If X be methyl, CH_3, that is to say, a group capable of replacing hydrogen because it is actually contained with hydrogen in methane itself, then by substituting this group for the original hydrogen, we obtain acetic acid, $CCH_3O(OH)$, out of formic, and by substitution of the hydrogen in its oxide or hydroxyl we obtain methyl formiate, $CHO(OCH_3)$. These bodies differ so much from each other physically and chemically that, at first sight, it is hardly possible to admit that they contain the same atoms in identically the same proportions. Acetic acid, for example, boils at a higher temperature than water, and has a higher specific gravity than it, while its metamer, formo-methylic ether, is lighter than water, and boils at 30°, that is to say, it evaporates very easily.

Let us now turn to carbon compounds containing two atoms of carbon to the molecule, as in acetic acid, and proceed to evolve them from methane by the principle of substitution. This principle declares at once that methane can only be split up in the four following ways :—

1. Into a group CH_3 equivalent with H. Let us call changes of this nature methylation.
2. Into a group CH_2 and H_2. We will call this order of substitution methylenation.
3. Into CH and H_3, which commutations we will call acetylenation.
4. Into C and H_4, which may be called carbonisation.

It is evident that hydrocarbon compounds containing two atoms of carbon can only proceed from methane, CH_4, which contains four atoms of hydrogen by the first three methods of substitution; carbonising would yield free carbon if it could take place directly, and if the molecule of free carbon—which is in reality very complex, that is to say, strongly polyatomic, as I have long since been proving by various means—could contain only C_2, like the molecules O_2, H_2, N_2, and so on.

By methylation we should evidently obtain from marsh gas, ethane, $CH_3CH_3 = C_2H_6$.

By methylenation, that is by substituting group CH_2 for H_2, methane forms ethylene, $CH_2CH_2 = C_2H_4$.

By acetylenation, that is by substituting three atoms of hydrogen, H_3, in methane, by the remnant CH, we get acetylene, $CHCH = C_2H_2$.

If we have applied the principles of Newton correctly, there should not be any other hydrocarbons containing two atoms of carbon in the molecule. All these combinations have long been known, and in each of them we can not only produce those substitutions of which an example has been given in the case of methane, but also all the phases of other substitutions, as we shall find from a few more instances, by the aid of which I trust that I shall be able to show the great complexity of those derivatives which, on the principle of substitution, can be obtained from each hydrocarbon. Let us content ourselves with the case of ethane, CH_3CH_3, and the substitution of the hydrogen by hydroxyl. The following are the possible changes :—

1. $CH_3CH_2(OH)$: this is nothing more than spirit of wine or ethyl alcohol, $C_2H_5(OH)$ or C_2H_6O.

2. $CH_2(OH)CH_2(OH)$: this is the glycol of Wurtz, which has shed so much light on the history of alcohol. Its isomer may be $CH_3CH(OH)_2$, but as we have seen in the case of $CH(OH)_2$, it decomposes, giving off water, and forming aldehyd, CH_3CHO, a body capable of yielding alcohol by uniting with hydrogen, and of yielding acetic acid by uniting with oxygen.

If glycol, $CH_2(OH)CH_2(OH)$, loses its water, it may be seen at once that it will not now yield aldehyd, CH_3CHO, but its isomer,—

$$\begin{matrix} CH_2CH_2 \\ O \end{matrix},$$

the oxide of ethylene. I have here indicated in a special manner the oxygen which has taken the place of two atoms of the hydrogen of ethane taken from different atoms of the carbon.

3. $CH_3C(OH)_3$ decomposed as $CH(OH)_3$, forming water and acetic acid $OH_3CO(OH)$. It is evident that this acid is nothing else than formic acid, CHO(OH), with its hydrogen replaced by methyl. Without examining further the vast number of possible derivatives, I will direct your attention to the circumstance that in dissolving acetic acid in water we obtain the maximum contraction, and the greatest viscosity, when to the molecule $CH_3CO(OH)$ is added a molecule of water, which is the proportion which would form the hydrate $CH_3C(OH)_3$. It is probable that the doubling of the molecule of acetic acid at temperatures approaching its boiling-point has some connection with this power of uniting with one molecule of water.

4. $CH_2(OH)C(OH)_3$ is evidently alcoholic acid, and, indeed, this compound, after losing water, answers to glycolic acid, $CH_2(OH)CO(OH)$. Without investigating all the possible isomers, we will note only that the hydrate $CH(OH)_2CH(OH)_2$ has the same composition as $CH_2(OH)C(OH)_3$, and although corresponding to glycol, and being a symmetrical substance, it becomes, on parting with its water, aldehyd of oxalic acid, or the glyoxal of Debus, CHOCHO.

5. $CH(OH)_2C(OH_3)$, from the tendency of all the preceding, corresponds to glyoxylic acid, aldehyd acid, CHOCO(OH), because the group CO(OH), or carboxyl, enters into the compositions of organic acids, and the group CHO defines the aldehyd function.

6. $C(OH)_3C(OH)_3$ through the loss of $2H_2O$ yields the bibasic oxalic acid, CO(OH)CO(OH), which generally crystallises with $2H_2O$, following thus the normal type of hydration characteristic of ethane.*

Thus, by applying the principle of substitution, we can, in the simplest manner, derive not only every kind of hydrocarbon compound, such as the alcohols, the aldehyd alcohols, aldehyds, alcohol acids, and the acids, but also

* One more isomer, $CH_2CH(OH)$, is possible, that is secondary vinyl alcohol, which is related to ethylene, CH_2CH_2, but derived by the principle of substitution from CH_4. Other isomers of the composition C_2H_4O, such, for example, as $CHCH_3(OH)$, are impossible, because it would correspond to the hydrocarbon $CHCH_3 = C_2H_4$, which is isomeric with ethylene, and it cannot be derived from methane. If such an isomer existed, it would be derived from CH_2, but such products are, up to the present, unknown. In such cases the insufficiency of the points of departure of the statical structural teaching is shown. It first admits constant atomicity, and then rejects it, the facts serving to establish either one or the other view; and therefore, it seems to me, that we must come to the conclusion that the structural method of reasoning, having done a service to science, has outlived the age, and must be regenerated, as, in their time, was the teaching of the electro-chemists, the radicalists, and the adherents of the doctrine of types. As we cannot now lean on the views above stated, it is time to ab ndon the structural theory. They will all be united in chemical mechanics, and the principle of substitution must be looked upon only as a preparation for the coming epoch in chemistry, where such cases as the isomerism of fumaric and maleic acids, when explained dynamically, as proposed by Le Bel and Van't Hoff, may yield points of departure.

combinations analogous to hydrated crystals which usually are disregarded.

But even those unsaturated, substances of which ethylene, CH_2CH_2, and acetylene, CHCH, are types, may be evolved with equal simplicity. With respect to the phenomena of isomerism, there are many possibilities among the hydrocarbon compounds containing two atoms of carbon, and without going into details it will be sufficient to indicate that the following formulæ, though not identical, will be isomeric substantially among themselves :—CH_3CHX_2 and CH_2XCH_2X, although both contain $C_2H_4X_2$, or CH_2CX_2 and CHXCHX, although both contain $C_2H_2X_2$, if by X we indicate chlorine or generally an element capable of replacing one atom of hydrogen, or capable of uniting with it. To isomerism of this kind belongs the case of aldehyd and the oxide of ethylene, to which we have already referred, because both have the composition C_2H_4O.

(To be continued).

ZIRCONIUM AND ITS ATOMIC WEIGHT.*

By G. H. BAILEY, D.Sc., Ph.D., The Owens College.

(Continued from p. 8).

Zirconium Peroxide, ZrO_3.

CLEVE (*Paris Soc. Chim. Bull.*, vol., xliii., p. 53) precipitated an oxide, to which he assigned the composition ZrO_3, by adding ammonia and hydrogen peroxide to a solution containing a zirconium salt; my own experiments (*Chem. Soc. Journ.*, vol xlix., p. 481), in which the oxide was precipitated from a dilute solution by the addition of hydrogen peroxide alone, the solution being slightly acid, gave an oxide agreeing well with the composition Zr_2O_5; it was found also that an oxide resembling Clève's could be obtained without the addition of ammonia. In order to see whether the peroxide, ZrO_3, was identical with that obtained by Clève, I precipitated a large quantity of a moderately concentrated solution of zirconium sulphate, containing a slight excess of acid—

(*a*). By the addition of hydrogen peroxide alone.
(*b*). By the addition of hydrogen peroxide, and then ammonia, until just alkaline.

	Mean determinations. (*a*).	(*b*).	Calculated for ZrO_3.
Zr	64·92	64·97	65·21
O	35·08	35·03	34·79

It is evident, therefore, that with due precaution an oxide agreeing very definitely with the formula ZrO_3 is obtainable by precipitation with hydrogen peroxide, either in alkaline or acid solution. The addition of ammonia, especially in excess, is, however, not to be recommended, since it tends to bring down the ordinary oxide, and to decompose the hydrogen peroxide added, with the production of nitrous and nitric acid. Dried for several weeks over phosphorus pentoxide, the oxide became constant in weight, and showed the composition $ZrO_3.3H_2O$, the hydrate of zirconia being $ZrO_2.2H_2O$. The salt, however, lost about 2 per cent of oxygen during the process of drying, and if this were carried out at 100° it had the composition Zr_2O_5.

Zirconium Tetrachloride.

About 30 grms. of this salt were prepared in the usual way, by passing dry chlorine over a mixture of charcoal and zirconia. If a determination was to be made from this salt some process of purification was necessary, and a criterion that a body of constant composition had been obtained, especially as it is known that volatile oxychlorides exist.

For this purpose a combustion-tube, in which the chloride was prepared, was drawn out into a series of bulbs, separated by constrictions. The chloride was then sublimed (a lower temperature being used for each successive bulb) in a current of dry chlorine into these bulbs, which were separately sealed off and their contents analysed. It was hoped in this way that two or more bulbs would be obtained showing concordant results, but, notwithstanding that every precaution was taken to exclude air and moisture, no such result could be achieved, and decomposition was clearly indicated to have taken place with the formation of traces of a reddish brown product, the equivalent of chlorine in relation to zirconium being in some cases higher and in others lower than four to one. Furthermore, in no case was it found possible to prepare such a product perfectly free from silica or iron. It seems, indeed, that zirconium tetrachloride is even more liable to dissociation and decomposition than the corresponding silicon compound.

Zirconium Oxychloride.

This salt is prepared, as already stated, by crystallisation from concentrated hydrochloric acid. The difficulties attending its preparation in the pure state arise from the presence of free hydrochloric acid and from the readiness with which the salt passes into oxychlorides of a more basic character. Berzelius attempted to remove the excess of free acid by heating the salt to 60°, but was not able to obtain a definite product, his numbers being—

ZrO_2	0·332	0·485
AgCl	0·661	1·096

whereas the silver chloride should be about 2⅓ times the amount of the ZrO_2. Paykull (*Paris Soc. Chim. Bull.*, vol. xx., p. 65) dried the salt between filter-paper, and found the composition of the crystals to be $ZrOCl_2.8H_2O$, the amorphous form precipitated by excess of HCl being $2ZrOCl_2.13H_2O$.

Basic oxychlorides, $Zr_3O_4Cl_4$ (Endemann), $Zr_2O_3Cl_2$, Zr_2OCl_6 (Troost and Hautefeuille), ZrOClOH, $Zr_8O_8Cl_7(OH)_9$ (Endemann), have also been described.

The salt examined by me was prepared by repeated crystallisation from concentrated hydrochloric acid, washed with hydrochloric acid till the washings were colourless and showed no trace of iron, and then the free acid removed—

(*a*). By washing with a mixture of 1 part of alcohol and 10 parts of ether.
(*b*). By gently heating the salt.
(*c*). By exposing the finely powdered salt at ordinary temperature in a vacuous desiccator over potash, until no HCl appeared when air was passed over it.

The analysis was performed by dissolving the salt in water and precipitating the zirconia with ammonia, then acidulating with nitric acid, and precipitating the chlorine by means of silver nitrate.

In the following tables are given Berzelius's determinations and those obtained by using the methods (*a*) and (*c*). (*b*) is omitted, since it was found that a constant and progressive diminution of chlorine occurred during the process. It will be sufficient for the purpose to state simply the relation of ZrO_2 to AgCl obtained.

	ZrO_2.	AgCl.
(1). Berzelius's determination	1 :	1·991
,, ,, ...	1 :	2·260
(*a*). Washed with ether and alcohol ..	1 :	2·206
	1 :	2·179
	1 :	2·226
	1 :	2·260
(*c*). Exposed *in vacuo* over KHO ..	1 :	2·264
Without washing	1 :	2·245
	1 :	2·309
	1 :	2·285
$ZrOCl_2$(Zr = 90)	1 :	2·350

* A Paper read before the Royal Society, May 9, 1889.

The whole of the specimens analysed dissolved in water to a clear solution, with a slightly acid reaction. The determination which shows the highest proportion of chlorine would give the atomic weight of zirconium as 92, which is, undoubtedly, too high, and, moreover, it will be quite evident from these numbers that no trustworthy determination was to be expected from this salt.

The Tetrabromide.

This salt was prepared by heating zirconium in an atmosphere of bromine vapour, but proved no more promising in its behaviour than the corresponding chlorine derivative.

The Sulphate.

Several methods of preparing the sulphate were tried, but ultimately that originally used by Berzelius was adopted. Finely powdered zirconia (air-dried) was heated with concentrated sulphuric acid, and most of the excess of acid driven off at as low a temperature as possible. In order to obtain the normal sulphate Berzelius drove off the excess of sulphuric acid, and then heated for a quarter of an hour, but never to redness; Mats Weibull heated till constant at 300°; a temperature manifestly too low. Clève, in a private communication, advised me to heat in a sulphur-bath (442°). It seemed, however, that in this instance, where the atomic weight depended on determinations from the sulphate alone, and especially since this is a general method applicable to several other elements, it was desirable that the limits of temperature within which the normal sulphate was stable should be ascertained. This was done in the case of a number of sulphates (Bi, Mg, Tn, Di), and the details of the investigation have already appeared (*Chem. Soc. Journ.*, vol. li., p. 676).

The salt containing excess of sulphuric acid was heated in a bath, described in that communication, which could be easily kept within 5°, at any temperature up to 500°. The boat containing the salt was weighed from time to time until it became nearly constant. The salt was then finely powdered, and the heating continued in periods of about four hours, until no further diminution of weight occurred, showing that the free sulphuric acid had been got rid of. The temperature of the bath was now raised by intervals of about 10°, and the heating continued for several hours at each limit, weighings being made after each increment until a point was arrived at at which loss of weight was again observed. This indicated that the temperature had been attained at which the normal salt began to undergo decomposition. We have then the limits of temperature within which the normal sulphate is stable. Several series of determinations were made, and one of these is given to show the character of the values obtained.

				Grms.
Weighing tube and boat				20·64962
,, ,, and salt				22·9095
After heating	6 hours	at 300°		22·9045
,,	7 ,,	330		22·9015
,,	4 ,,	350		22·9002
,,	4 ,,	365		22·90012
,,	5 ,,	380		22·90025
,,	4 ,,	390		22·90020
,,	4 ,,	410		22·89820

The above numbers have not had applied to them the small corrections for variations of barometer and thermometer, and no importance need be attached to the differences of one- or two-tenths of a m.grm. between 350° and 400°.

It appears, therefore, from these experiments that zirconium sulphate is stable up to 400°, and that the excess of sulphuric acid is driven off completely at 350°. If, therefore, a mixture of the salt and the free acid, prepared as above, be heated at any temperature between 350° and 400° till constant, we shall obtain the normal sulphate. The temperature of the sulphur-bath would be too high, and of course at dull redness decomposition would set in.

(To be continued).

ON THE

OCCURRENCE OF PARAFFIN IN CRUDE PETROLEUM.*

By E. A. PARTRIDGE, University of Pennsylvania.

It is well known that paraffin obtained by the distillation of petroleum residues is crystalline, while that obtained directly (as in the filtration of residuum) is amorphous. Ozokerite or ceresine differs but slightly from paraffin, the principal distinction being want of crystalline structure in it as found. Other characteristics, such as the melting-point, specific gravity, &c., vary in both, and so are not of importance in a comparison. Hence it has been asked, is the paraffin occurring in petroleum and ozokerite identical with that which is produced by their distillation? As crystalline paraffin could be obtained from ozokerite by distillation alone, many persons have supposed that it was engendered in the process. Recently, however, crystalline paraffin has been obtained from ozokerite by dissolving the latter in warm amyl alcohol; on cooling, the greater part separates out in crystals having the lustre of mother-of-pearl. By repetition of this process, a substance is obtained that is scarcely to be distinguished from the paraffin obtained by distillation. Apparently there exists then in ozokerite, together with paraffin, other substances not capable of crystallisation which keep the paraffin from crystallising. These colloids appear to be separated by amyl alcohol in virtue of their great solubility in that menstruum. It is also reasonable to suppose that they undergo change or decomposition by distillation.

So as petroleum residues are amorphous, and the crystalline paraffin is first produced by distillation, it has been argued that the paraffin present in crude petroleum is approximately the same thing as ozokerite.

This, however, is not sufficient to establish the pyrogenic origin of all crystallised paraffin, as crystals can be obtained from the amorphous residues by distillation at normal or reduced pressure, or in a current of steam. To explain these facts two assumptions are possible. Either the chemical and physical properties of all or some of the solid constituents are changed by the distillation, and the paraffin is changed from the amorphous into the crystalline variety, or the change produced by the distillation takes place in the medium (*i.e.*, the mother liquid) in which the paraffin exists. The change effected in ozokerite and in petroleum residues when crystalline paraffin is obtained by distillation, is to be regarded as a purification, and can be effected partly by treatment with amyl alcohol. In the same way, by repeated treatment of petroleum residuum with amyl alcohol, a substance of melting-point 59° C. can be obtained, which cannot be distinguished from ordinary paraffin.

The treatment with amyl alcohol has therefore accomplished the same results as were obtained by distillation, and the action is probably the same, *i.e.*, a partial separation of colloid substance. These facts point to the conclusion that crystallisable paraffin exists ready formed in both petroleum and in ozokerite, but in both cases other colloidal substances prevent its crystallisation. By distillation, these colloids appear to be destroyed or changed so as to allow the paraffin to crystallise.

It is a generally known fact that liquids always appear among the products of the distillation of paraffin, no

* An Abstract of a Thesis read before the Chemical Section of the Franklin Institute.

matter in what way the distillation be conducted. This shows that some paraffin is decomposed in the operation.

The name *proto-paraffin* has been given to ozokerite, and to the paraffin of petroleum in contra-distinction to *pyro-paraffin*, the name that has been applied to the paraffin obtained by distillation from any source.

According to Reichenbach, paraffin may crystallise in three forms: needles, angular grains, and leaflets having the lustre of mother-of-pearl. Hofstädter, in an article on the identity of paraffin from different sources, confirmed this statement, and added, further, that at first needles, then the angular forms, and then the leaflets are formed. Fritsche found, by means of the microscope, in the ethereal solution of ozokerite, very fine and thin crystal-leaflets concentrically grouped, and in the alcoholic solution fine irregular leaflets. Zaloziecki has recently developed these microscopic investigations to a much greater extent. According to this observer, the principal part of paraffin, as seen under the microscope, consists of shining stratified leaflets with a darker edge. The most characteristic and well-developed crystals are formed by dissolving paraffin in a mixture of ethyl and amyl alcohols, and chilling. The crystals are rhombic or hexagonal tablets or leaves, and are quite regularly formed. They are unequally developed in different varieties of paraffin. The best developed are those obtained from ceresine. Their relative size and appearance give an indication as to the purity of the paraffin, and, as they are always present, they are to be counted among the characteristic tests for paraffin. Reichenbach observed that mere traces of empyreumatic oil prevented their formation.

The old method of determining the amount of paraffin in petroleum was to carry out the refining process on a small scale; that is, to distil the residue from the kerosene oils to coking, chill out the paraffin, press it thoroughly between filter-paper, and weigh the residue. The sources of error in this procedure are manifold; the principal one is the solubility of paraffin in oils, which depends upon the character of both the paraffin and the oil, and also upon the temperature. The next greatest source of error is variation in the process of distillation, and the difference between working on the small scale and on the large scale.

In most cases, where a paraffin determination is to be carried out, one has to deal with a mixture of paraffin with liquid oils. Now, paraffin is not a substance defined by characteristic physical properties which distinguish it from the liquid portions of petroleum. It consists of a mixture of homologous hydrocarbons, which form a solid under ordinary conditions. The hydrocarbons of this mixture show a gradation in their properties, and gradually approximate to those which are liquid at ordinary temperatures. It is a well-known fact that a separation of these homologues is entirely impossible by distillation. It has also been ascertained that the liquid constituents of petroleum do not always possess boiling-points that are lower than those of the solid constituents. This shows that we have to deal not merely with hydrocarbons of one but of several series.

When determinations of the amount of paraffin are to be made, then it becomes necessary to specify with exactness what is to be called paraffin. The most definite property that can be made use of for this purpose is the melting point. For several reasons it is convenient to include under this name hydrocarbons of melting-point as low as 35°—40° C.

The method proposed by Zaloziecki for the determination of paraffin is the following:—The most volatile portions of the petroleum are separated by distillation, until the thermometer shows 200° C. These portions are separated, as they exert great solvent action upon paraffin. At the same time, he finds that no pyro-paraffin is formed under this temperature. A weighed portion of the residue is taken and mixed with ten parts by weight of amyl alcohol and ten parts of 75 per cent ethyl alcohol; the mixture is then chilled for twelve hours to 0° C. It is then filtered cold, washed first with a mixture of amyl and ethyl alcohols, and then with ethyl alcohol alone. The paraffin is transferred to a small porcelain evaporating dish and dried at 110° C. It is then heated with concentrated sulphuric acid to 150°—160° C. for fifteen to thirty minutes with constant stirring. The acid is then neutralised and the paraffin extracted by petroleum ether. On evaporation of the solvent, the paraffin is dried at 100° C., and weighed. Zaloziecki found, according to this method, in three samples of Galician petroleums, 4·6, 5·8, and 6·5 per cent, respectively, of proto-paraffin. The method was carried out as above, with four samples of American petroleums, Colorado oil from Florence, Col.; Warren County oil from Wing Well, Warren, Pa.; Washington oil from Washington County, Pa.; Middle District oil from Butler County, Pa., all furnished by Professor Sadtler.

They were very different in physical properties and in appearance, the Colorado oil being a much heavier oil than the others, and the Washington oil being an amber oil, while the other two were of the ordinary dark green colour and consistence. The losses on distillation to 200° C. were very different, being about one-tenth in the case of the Colorado oil, and nearly one-half in the case of the others. The percentages of partially refined proto-paraffin in the four reduced oils (all below 200° C. off) were as follows:—For the Colorado oil, 23·9 per cent; for the Warren oil, 26·5 per cent; for the Washington oil, 26·6 per cent; and for the Middle District oil, 28·2 per cent.

The question now arises, what value has this determination of the proto-paraffin which may exist in an oil? As before said, a portion of the paraffin is always decomposed in distillation at temperatures sufficiently high to drive over the paraffin oils, so the yield of pyro-paraffin is always less than the proto-paraffin shown to be present originally. Zaloziecki found this in the case of the several Galician oils he examined. Corresponding to the 4·6, 5·8, and 6·5 per cent of proto-paraffin in the several oils, he obtained 2·18, 2·65, and 2·35 per cent, respectively of pyro-paraffin.

For the present, however, the extraction of proto-paraffin on a large scale by means of such solvents as amyl and ethyl alcohols is out of the question on account of their cost. A distillation, under reduced pressure and with superheated steam, would, however, prevent much of the decomposition of the original proto-paraffin and increase the yield of pyro-paraffin.

This study of Zaloziecki's method and the examination of American oils was suggested by Professor Sadtler, and carried out in his laboratory.

THE DETERMINATION OF SULPHURIC ACID IN PRESENCE OF IRON.

By P. JANNASCH and T. W. RICHARDS.

It has long been known that the precipitation of barium sulphate in presence of iron salts gives very irregular results. As far back as 1877 Fresenius proposed to fuse pyrites with a mixture of sodium carbonate and potassium nitrate, and to determine the sulphuric acid in the filtrate from the watery extract of the melt. Lunge regarded this method as too complicated and tedious, and preferred to dissolve the mineral in nitro-hydrochloric acid, and to remove impurities from the precipitate by subsequent treatment with hydrochloric acid.

The authors, on a re-examination of the question, attempted to convert any ferric salts present into the ferrous state by reduction with sodium amalgam, metallic magnesium, or zinc. The results were so unsatisfactory

that this idea had to be abandoned. Iron was not absent in the precipitate, and the oxide of the reducing metal was also present.

Special experiments were made to decide if the presence of organic acids (citric, acetic, or formic) would prevent the precipitation of iron. The results were not satisfactory, and the barium sulphate obtained had the usual reddish tone. The error is in the first place a function of the iron simultaneously present, which falls out rather smaller with ferrous than with ferric salts. It was established that barium sulphate is not soluble in cold ferric solutions, and though somewhat soluble in hot ferric solutions it is re-deposited on cooling.

Attempts were made to remove the iron from the barium sulphate by digesting with hydrochloric acid before ignition. The precipitate was washed by decantation, digested for a considerable time with an excess of ammonium sulphide, and then treated with very dilute hydrochloric acid. The barium sulphate, however, had a reddish colour after ignition.

It appears that the iron is thrown down as a double compound with barium, barium-ferric sulphate, which is decomposed only at bright redness.

The experiments show that in presence of iron an accurate determination of sulphuric acid by direct precipitation with barium chloride is not practicable. For a correct analysis of pyrites the soda-nitre melting process of Fresenius is the only accurate method. The result of the titration of sulphuric acid in presence of iron with barium chloride must be abandoned, since the double iron-barium sulphate is thrown down, and too little barium chloride is consumed.—*Journal fur Praktische Chemie*, New Series, vol. xxxix., p. 321.

ON THE

PREPARATION AND PROPERTIES OF METALLIC MANGANESE.*

By CHARLES BULLOCK.

The properties of manganese, like those of iron, appear to differ according to the method used in the reduction of the metal. When obtained from the oxide by heating with carbon, most authorities agree in the statement that the metal oxidises so readily in the air that it can be preserved only under "rock oil," or in well sealed vessels. In water it is said to "oxidise rapidly, with evolution of hydrogen, and crumbles into a dark grey powder."

Cast manganese containing eight per cent of iron is said to be unalterable in the air.

In the year 1869, some manganese prepared after the process of Brunner (the reduction of the chloride mixed with fluor-spar, by means of sodium) was found to have as little tendency to oxidation as iron.

Repeating recently this process, pure chloride of manganese was fused in a clay crucible and poured on a stone slab; when cold it was pulverised and mixed with an equal weight of powdered fluor-spar. This mixture, divided into portions of one ounce, was introduced into a French clay crucible, previously heated to redness. Eighty grains of sodium, cut into small pieces and freed from naphtha, being added to each portion, the crucible was covered, and reaction allowed to take place before adding another charge. After six ounces of the mixture had been added, the contents of the crucible was covered with fused chloride of sodium in powder, the cover replaced, and the heat carried to quiet fusion. After the flux became entirely fluid the heat was continued for ten minutes. The crucible was then removed from the fire, and, after cooling, the metal was found as a button at the bottom.

Three crucibles, of the capacity of eight fluid ounces each, were used at a time in a furnace without artificial blast. Care is necessary not to urge the heat too high, otherwise the crucibles will not resist the action of the fluor-spar flux. The French clay crucibles (Beaufay) were used on account of their greater freedom from iron and silica; they also resist the flux better than the Hessian, black-lead, or iron crucibles.

The yield of manganese under favourable circumstances was about twenty per cent of the chloride used.

Reduction was also tried by using fused chloride of sodium without fluor-spar, the yield of metal was much less, and differing in some of its properties from that obtained with the use of fluor-spar. Manganate of soda was formed when sodium chloride alone was used as a flux.

Manganese thus obtained is very brittle, with a steel white fracture, so hard that a file will scarcely touch it; the edges of the fractures scratch and almost cut glass.

The metal retains the brightness of a fractured surface after prolonged exposure to the air, and appears not more disposed to oxidation than iron. It is entirely passive to magnetic attraction.

The specific gravity of the metal obtained when fluor-spar was used was 7·072, when re-melted under fused sodium chloride the specific gravity rose to 7·153.

The metal obtained without the use of fluor-spar was less brittle, and had a different fracture; its sp. gr. was 7·231.

Authorities differ regarding the sp. gr. of manganese, ranging it from 6·85 to 8·013.

An examination of the metal obtained, using fluor-spar as a flux, showed the absence of iron and the presence of calcium, demonstrating the reduction of some of the latter metal from the spar. This may account in a measure for the increased sp. gr. on re-melting under sodium chloride, as also the greater sp. gr. of the metal when the spar was not used. As calcium has the sp. gr. of 1·57, a small amount alloyed with the manganese would sensibly affect its gravity.*

THE INFLUENCE OF SILICON ON THE DETERMINATION OF PHOSPHORUS IN IRON.†

By THOMAS M. DROWN, Professor of Analytical Chemistry in the Massachusetts Institute of Technology, Boston.

The process for determining phosphorus in iron now in most general use in the laboratories of iron and steel works is, I think, the one proposed by Mr. Emmerton.‡ In this process the solution of the iron for precipitation by ammonium molybdate is effected by treating the iron with nitric acid, evaporating to hard dryness in a dish, taking up with hydrochloric acid, and driving off the greater portion of the hydrochloric by nitric acid. This procedure accomplishes, first, the destruction of all the carbonaceous matters; and, second, renders all the silica insoluble.

Experience has proved the former—the complete oxidation of the carbon—to be absolutely essential; but the explanation usually given, namely, that unless the carbon compounds are destroyed they will have a solvent action on the yellow precipitate, I am inclined to doubt. It seems to me more probable, as suggested by Mr. P. W. Shimer, that the conditions which are favourable for the oxidation of the carbon compounds ensure the complete oxidation of the phosphorus to ortho-phosphoric acid, and that the reason of the imperfect precipitation of the phosphorus, when the solution of the iron in nitric acid is directly precipitated by molybdate solution, is that the phosphorus is not completely oxidised.

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* Read at the Meeting of the Chemical Section of the Franklin Institute, May 21, 1889.

* Sp. gr. of iron—gray, 7·1; white, 7·5; pure, 7·84.

† *Transactions of the American Institute of Mining Engineers*, vol. xviii.

‡ *Ibid*, xv., 93.

There have been many means proposed for destroying the carbon compounds—chromic acid, potassium chlorate, potassium permanganate, hydrogen peroxide, and others which accomplish the purpose without the necessity of evaporating the solution to dryness. The advantage of the latter method, however, has been supposed to be that in this way the silica was at the same time rendered insoluble.

The statement of Klein* that, in the determination of phosphoric acid in basic slag, it is not necessary to separate the silica, since the ammonium silico-molybdate is soluble in 3 per cent nitric acid, led me to try the effect of precipitating the phosphorus in a solution of pig-iron without previously evaporating to dryness. The results agreed perfectly with others obtained in the usual way after the removal of the silica; and further investigation showed that the silicon, at least in the form in which it exists when pig-iron is dissolved in nitric acid, is not precipitated by the molybdate solution.

There is a very marked difference in the effect of nitric acid of different strengths on pig-iron, as regards the condition of the silicon. When the acid is strong (1·2 to 1·4 sp. gr.) much of the silicon becomes gelatinous and prevents filtration, while with more dilute acid the silicon goes almost entirely into solution.

In a former communication to the Institute† I gave the effect of different strengths of hydrochloric acid on the silicon in pig-iron, showing that the strongest acid renders nearly all the silicon insoluble, and that weak acid dissolves it almost entirely. Generally speaking, the same is true, also, of nitric acid, as the following determinations show. It is interesting to note in the following figures that a nitric acid of medium strength dissolves more silicon than acid either stronger or weaker.

The pig-iron used in the following tests was a No. 1 foundry-iron, containing 2·42 per cent silicon.

Effect of Nitric Acid of Different Strengths on the Silicon in Pig-iron.

Acid. Sp. gr	Silicon, per cent. In graphitic residue.	Silicon, per cent. In solution.
1·4	2·28*a*	0·14
	2·01*a*	0·34
1·2	0·75*a*	1·67
	0·44*a*	1·98
1·16	0·07	—
	0·07	—
1·135	0·07	—
	0·06	—
	0·06	—
	0·06	
1·116	0·09	—
	0·11	—

Acid. Sp. gr	Silicon, per cent. In graphitic residue.	Silicon, per cent. In solution.
1·102	0·12	
	0·12	—
	0·12	—
	0·12	—
	0·13	—
1·082	0·23	—
	0·23	—
	0·23	—
1·070	0·20	1·12
	0·24	—
	0·27	2·14
	0·31	2·12

a By difference.

The solutions obtained with the use of acid of 1·4 and 1·2 sp. gr. could not be filtered in concentrated condition, owing to the gelatinous form of the silica. They were, therefore, largely diluted, and an aliquot portion of the solution was obtained by filtration. In this the silicon was determined.

The solutions obtained with acid of 1·116 sp. gr., and still more dilute, can be filtered without difficulty,

The separation of gelatinous silica is not wholly a matter of strength of acid, neither is it wholly a matter of the percentage of silicon in the pig-iron. It has often been noted that different pig-irons, under identical treatment with nitric acid, will filter at different rates; and sometimes the iron with least silicon proves most refractory in filtering. This suggests that silicon may exist in different conditions in pig-iron, a subject which cannot be further discussed in this paper.

Another pig-iron was tested in this series of experiments—a grey forge iron, containing 0·63 per cent of silicon—with the following results:—

Silicon in Graphitic Residue.

	Per cent.
Acid, sp. gr. 1·2	0·19
	0·20
Acid, sp. gr. 1·135	0·03
	0·03
	0·05
	0·06

From the foregoing it will be seen that the strength of nitric acid most favourable for the solution of pig-iron is about 1·135 sp. gr., and not 1·2, which is generally used.* In the solution thus obtained there is no tendency of the silica to separate; not until the solution has been concentrated, by boiling to small bulk, does the silica begin to gelatinise.

When molybdate solution is added to a solution of pig-iron obtained in this way, the phosphorus, as might be expected, is but partially precipitated, because this treatment with nitric acid is insufficient to oxidise all the carbonaceous matter; or, as I prefer to believe, insufficient to oxidise all the phosphorus to ortho-phosphoric acid. To effect this object any of the oxidising agents already mentioned may be used. Potassium permanganate, as prepared by Shimer,† seems to me the most convenient; but for the solution of the separated manganese peroxide I use, instead of hydrochloric acid, a small quantity of some organic substance, such as tartaric, citric, or oxalic acid, or sugar. The manganese oxide disappears almost immediately on the addition of the organic matter. After this treatment, which requires only a minute or two, the molybdate solution will give a complete precipitation of the phosphorus.

The following determinations were made in order to discover whether there is any tendency for the silicon in solution to be carried down with the yellow precipitate, either mechanically or as silico-molybdate. The pig-iron used was that already mentioned, containing 2·42 per cent silicon.

Silicon determined.	I. P.c.	II. P.c.	III. P.c.	IV. P.c.
In residue from nitric acid solution	0·040	0·040	0·070	0·100
In yellow precipitate ..	0·030	0·050	0·012	0·012
In washings of the yellow precipitate with 2 per cent nitric acid	0·050	0·030	0·007	0·004
In filtrate from the yellow precipitate	2·250	2·210	2·340	2·280
Total	2·370	2·330	2·429	2·396

There seems to be, then, no evidence of the formation of any precipitate of ammonium silico-molybdate.

If the separation of the silica is omitted, the determination of phosphorus in pig-iron may be carried out in very much less time than is ordinarily required. In the laboratory of Massachusetts Institute of Technology we have adopted the following procedure:—About 1·5 grms. of the pig-iron (or more if very low in phosphorus) is treated in a covered beaker with 60 c.c. of nitric acid of 1·135 sp. gr. (If preferred, 20 c.c. of water may be first added, and then 40 c.c. of nitric acid, sp. gr. 1·2. In this variation the action is at first a little less violent). The

* *Chem. Zeitung*, x., 721.

† *Transactions of the American Institute of Mining Engineers*, viii., p. 514.

* Acid of 1·135 sp. gr. is conveniently made by diluting acid of 1·2 sp. gr. with half its bulk of water, or by diluting 1·4 sp. gr., and with water in the proportion of 3 to 7.

† *Transactions of the American Institute of Mining Engineers*, xvii.

beaker is heated on an iron plate until action ceases; three minutes is usually sufficient time if the borings are reasonably fine. The solution is then filtered from the graphite into a 500 c.c. flask, and to the boiling filtrate is added 15 c.c. of permanganate solution of 5 grms. to the litre.* Boiling is continued until the pink colour has disappeared, and a few very small fragments of tartaric acid are then added, causing the precipitated manganese peroxide to go almost immediately into solution. The amount of tartaric acid need not exceed 0·1 grm., although the addition of an excessive quantity—as much as 1 grm.—does not influence the results perceptibly. To the clear solution 10 c.c. of strong ammonia (sp. gr. 0·90) are added to partially neutralise the free nitric acid. This amount leaves the solution still amber-coloured; it should not be so far neutralised as to become wine-coloured. When the solution has cooled down to 90° C., 80 c.c. of molybdate solution† is added, and the flask is closed with a rubber stopper, wrapped in a towel and shaken vigorously for five minutes, as recommended by Emmerton. From this point on the directions of Emmerton, in his paper already mentioned, are followed, namely, reduction by zinc and titration by permanganate. If fine powdered zinc is used it may be entirely dissolved in about ten minutes, but filtration from the undissolved zinc seems generally to be preferred.

The following results were obtained in this way on the sample of pig-iron containing 2·42 per cent of silicon, in comparison with the older method of dissolving the iron in nitric acid, evaporating to dryness to separate silica, and precipitations by molybdate solution and magnesia mixture.

No. 1 Pig-iron containing 2·42 per cent Silicon.

Phosphorus Determinations.

By the Old Method. Per cent.	By the New Method. Per cent.	By the New Method (Contd). Per cent.	Per cent.
0·284	0·272	0·297	0·286
	0·279	0·296	0·294
	0·290	0·289	0·294
	0·280	0·291	0·288
	0·291	0·291	0·292
	0·292	0·278	0·288
	0·289	0·294	
	0·292	0·293	

The rate of oxidation of the reduced molybdenum sesquioxide, on exposure to the air, is very slow, and is not ordinarily taken into account. Mr. J. W. Loveland found that it amounted, in this series of experiments, to 0·001 per cent of phosphorus for every ten minutes' standing before titration with permanganate. All the foregoing results have been corrected accordingly.

If rapidity of determination is of the first importance, a few minutes may be saved by omitting the filtering off of the graphite. Many trials show that this omission does not affect the accuracy of the results, although the removal of a foreign insoluble substance from the liquid enables one to carry out the process with greater satisfaction.

The following determinations of the phosphorus in the sample of gray-forge iron containing 0·63 per cent silicon were made without filtering off the graphite by Mr. Greeley, a student at the Massachusetts Institute of Technology.

Gray-forge Iron containing 0·63 per cent Silicon.

Phosphorus Determinations.

By the Old Method. Per cent.	By the New Method, without filtering from graphite. Per cent.	Per cent.
0·632	0·620	0·627
0·635	0·625	0·629
	0·631	0·645
	0·640	0·635
	0·633	

Two determinations made in the solution of the same pig-iron, after filtering from the graphite, gave 0·636 and 0·631. Further results obtained by Mr. Greeley are given below:—

Bessemer Iron containing 1·18 per cent Silicon.

Phosphorus Determinations.

By the Old Method. Per cent.	By the New Method. Per cent.
0·084	0·083
0·087	0·085
	0·086
	0·086
	0·085

No. 1 Pig-iron containing 2·29 per cent Silicon.

Phosphorus Determinations.

By the Old Method. Per cent.	By the New Method. Per cent.
0·334	0·324
0·330	0·327
	0·334
	0·324
	0·322

The process for steel is, of course, the same as for pig-iron, except that the question of filtration from graphite does not arise.

In a sample of Bessemer steel the following percentages of phosphorus were obtained.

By the Old Method. Per cent.	By the New Method. Per cent.
0·061	0·064
	0·060
	0·061

By one familiar with the details of the process, a determination of phosphorus in pig-iron can be easily made in less than an hour.

I am indebted to Mr. James W. Loveland, Assistant in Chemical Analysis in the Institute of Technology, for valuable aid in this investigation; the credit for the analytical work, except as otherwise mentioned, is due entirely to him.

* The strength of this solution is not a matter of importance; I have found the above amount sufficient. Shimer uses 10 c.c. of a solution of 20 grms. to the litre.

† Made by dissolving 100 grms. of molybdic acid in 400 c.c. ammonia, sp. gr. 0·96, and adding 1000 c.c. nitric acid, sp. gr. 1·2.

NOTICES OF BOOKS.

The Metallurgy of Silver. A Practical Treatise on the Amalgamation, Roasting, and Lixiviation of Silver Ores, including the Assaying, Melting, and Refining of Silver Bullion. By M. Eissler, Mining Engineer and Metallurgical Chemist, formerly Assistant Assayer of the U.S. Mint, San Francisco. London: Crosby Lockwood and Son.

A short time ago we had the pleasure of noticing Mr. Eissler's excellent work on the metallurgy of gold, and we now welcome its companion treatise as equally practical, comprehensive, and trustworthy. The predominant, if not exclusively, American character of the author's experience is here no drawback, since in modern times an overwhelming excess of the world's supply of silver has been drawn from the Western Hemisphere. Asia and Africa—whatever may have been the case, *e.g.*, in the days of Solomon—scarcely figure as silver-producing regions at all. Australia yields an increasing supply, the ultimate extent of which is still problematical; whilst Europe furnishes about 14 per cent of the whole. Thus silver-mining with its accessory operations may be viewed substantially as American industries.

In the outset of the volume the author gives, from the eminent geologist Clarence King, a most instructive summary of the metallic deposits of Western North America.

The methods here considered for effecting the separation of silver from its ores are two, the amalgamation process —wet or dry—and lixiviation. Other methods, suitable for different classes of silver ores, will be discussed in a future work.

We are compelled to enter a protest against a misuse of language met with in the preface. Says Mr. Eissler (p. 6), "Of late years a new *science* has been developed in the treatment of silver ores which cannot be worked profitably by amalgamation, &c." That a new *art* has arisen is admitted, but a new *science* is inconceivable, unless some novel category of phenomena is detected which has hitherto escaped human observation, or unless man becomes endowed with a new sense.

The author takes up systematically the different processes, and describes them, not as a compiler from the writings of others, but from personal, prolonged, and extended observation. The Patio process, he considers, could not be profitably superseded by any other where labour is cheap, the ores are poor, and fuel, and even water-power, is scarce. The loss of mercury is its great drawback, and this is reduced at Guadelupe y Calvo by the use of copper amalgam.

The "Washoe process" is described as used on the Comstock lode. A brief mention is made of absurd ingredients added by unchemical operators to facilitate amalgamation. Among these figure tobacco-juice and decoction of sage-bush. Even the addition of copper sulphate and common salt is of doubtful benefit. In some mills both these ingredients are used, in others salt alone, and in others again, neither, and yet the results are described as equally good. The machinery used in crushing and amalgamating is clearly described and illustrated by a number of figures drawn to scale.

The fourth chapter gives a full conspectus of the cost and result of milling operations. The total cost of treating a ton of ore is given as £1 14s., but where water-power is available it may fall below £1. The loss of mercury is considerable. It is even carried by escaping steam to the roof of the mill. If contaminated with copper it becomes coated with iron. It is also coated with iron pyrites, grease, and slimes. As a cleansing agent potassium cyanide is recommended. Ores containing talc have an unfavourable effect on the mercury. Manganese dioxide is a most objectionable ingredient of ores, occasioning heavy loss of quicksilver.

Chapter V. gives an account of the treatment of slimes and tailings, an important subject, as they sometimes contain a very considerable proportion of silver.

The dry process is next followed through its several stages of chlorinising, roasting, and amalgamation, and the necessary plant is duly figured.

The treatment of silver ores by lixiviation forms the subject of Chapter XIII. The modifications devised by Augustin, Ziervogel, and Russell are duly described. The comparative advantages of this modification as compared with amalgamation are fully explained. It requires a cheaper plant, it requires less mechanical power, saves the capital locked up in the stock of mercury, extracts a much higher proportion of silver, and, unlike amalgamation, it does not interfere with the health of the workmen.

The last chapter is devoted to the operations of assaying by the dry and the wet method, and refining. For bullion, alloys, &c., the author decidedly prefers the Gay-Lussac (volumetric) assay. He remarks that should appreciable quantities of non-oxidisable metals be present the dry assay is not available.

To all persons connected with or interested in the metallurgy of silver, this work will prove indeed a boon, giving, as it does, an account of all the most recent improvements by a writer who thoroughly understands his subject.

Inorganic Chemistry. By IRA REMSEN, Professor of Chemistry in the Johns Hopkins University. London Macmillan and Co.

As regards its extent and scope, this work occupies a medium rank between those short manuals or cram-books which have been produced of late years in such alarming numbers, and the encyclopædic treatises of Gmelin, Watts, or Roscoe and Schlorlemmer. As a favourable feature, we most notice that Prof. Remsen has not arranged his teaching to suit any "syllabus," nor does he address himself specially to students preparing for some examination. Neither does he furnish lists of papers which have been set, or questions which have been put by any college or department. He aims at teaching chemistry, leaving it to his readers to apply the facts and the laws laid down to any particular purpose required A peculiarity of the work, which, upon the whole, may be called advantageous, is that the experiments used in illustration and the apparatus needed for their performance are described and figured, not in the text, but in an appendix.

The classification of the elements has been carried out in accordance with the periodic system. In speaking of this system, the author certainly admits the priority of Mr. J. A. R. Newlands, but he seems to us to underrate his share in the discovery. He writes :—"Newlands's arrangement was quite imperfect." We can of course understand a system or an arrangement being "quite perfect" or "very imperfect," but we fail to see how a relative attribute, such as imperfection, can be qualified by any word which implies absoluteness.

We are pleased to find that Prof. Remsen recognises that the two departments of chemistry commonly known as the static and the dynamic or kinetic, bear to each other relations similar to those existing between morphology and physiology.

The author does not enlarge on questions which are as yet under investigation. On the possible origin and relations of the elements he is silent, accepting them as ultimate in the light of our present knowledge.

Although the work deals mainly with general principles, the practical and technical applications are by no means overlooked. The author's remarks on the waters of rivers, when used for domestic purposes, are exceedingly good, and show a judicious avoidance of extreme views. He writes :—"River-water, when once contaminated by drainage, tends to become pure again by contact with the air. . . . If the water is to be used for drinking purposes, however, it is not well to rely too much upon this process of purification. So much attention has of late years been given to the subject of drinking-water, that water is no doubt frequently held responsible for sickness with which it has little or nothing to do. In some places the war against the water-supply has been carried so far that those who can afford it drink only artificially purified and distilled water. It is undoubtedly well to be cautious, but it is possible to be too cautious." Prof. Remsen admits that chemical analysis cannot, in all cases, detect minute traces of extremely injurious substances.

Generally speaking it may be said that whoever wishes to obtain a correct and clear view of the principles of chemical science without entering into minute details will find this work admirably suited to his purpose.

An Elementary Treatise on Heat. By H. G. MADAN, M.A., F.C.S. London: Rivingtons.

IN his preface the author recommends a study of the phenomena and the laws of heat as "a very suitable and fruitful subject for school instruction." Very justly he recommends such instruction to be given to boys before they proceed to the more difficult study of chemistry. In justification of the expression "more difficult" he drily adds, in a note :—"If, that is, the subject is to be treated in a really scientific spirit, and not merely as an excuse

for producing brilliant effects of light and colour, startling explosions, and unsavoury smells." He declares that the laws of heat seem worthy of better treatment than to be considered as little more than subjects upon which arithmetical questions may be set for the purposes of a competitive examination (after the manner of numerous text-books of the present day)." Here, indeed, is a danger connected with the introduction of numerical exercises in courses of instruction in any branch of physical or natural science—that they are made to play into the hands of the examinational system, and to divert the mind of the student from the most important lessons which such studies ought to impart. The author employs, indeed, mathematical formulæ, but "only after a full statement in ordinary language of the facts which they express." In speaking of experiments before a juvenile auditory he gives a needful caution. "The work of science-lecturers often seems to be little more than a perpetual struggle against the malice of nature. Not a few interesting experiments have to be omitted, even by skilled lecturers, as too tedious or too uncertain for the conditions of a lecture-room. Here he adds a footnote which is too good not to be reproduced. M. Regnault was once asked by an eminent English chemist how he succeeded in the manipulation of a certain experiment which was very graphically described in his 'Cours Elémentaire de Chimie.' He replied:—'*Monsieur, c'est une expérience qu'on ne fait pas.*'"

After an introductory chapter the author discusses the nature of heat, its sources, natural and artificial, its effects upon substances, the measurement of temperature, the measurement of quantity of heat, the phenomena connected with change of state, the transmission of heat by conduction, convection, and radiation, the relations between heat and mechanical motion, and heat-engines. In conclusion we find a notice of the depreciation—commonly called "degradation"—of energy. Heat, unfortunately, is the socialist of the physical world, always seeking to run down to a dead level, and so far we have not been able to convert heat into other forms of energy without very great loss. Mr. Madan happily compares heat to a security in the money market, "which, though its intrinsic value may be great, yet cannot be converted into cash except at a ruinous loss, and is therefore depreciated in value." We do not know an elementary work on heat which we could recommend as preferable to the one before us.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cviii., No. 24, June 17, 1889.

The Combustion and Formation Heats of the Nitrites.—MM. Berthelot and Petit.—The authors consider the nitrites as the type of the compounds, capable of furnishing heat by simple hydratation over and above any phenomenon of oxidation. This result they consider very important as regards animal heat. The values due to hydratation exceed one-third of the combustion heat of the carbon contained in the organic compound.

The Thermo-chemical Method Summarised in its Principles and Results.—M. Sappey.—This is not a chemical paper, but the explanation of a method proposed for microscopic anatomical research.

On a New Method of Preparing the Alkaline Nitrates.—G. A. Le Roy.—The usual means of preparing these nitrites are the decomposition of the corresponding nitrates by a limited heat, their partial deoxidation by perfectly oxidisable bodies, such as graphite, reduced copper or lead (dry way) zinc powder, finely divided lead (moist way), alkaline sulphites, &c. The author's novel method is to cause two mols. of the alkaline nitrate to react with one mol. barium sulphide. The sulphide is reduced to a fine powder, intimately mixed with the nitrate, and the mixture is projected with constant stirring into an iron basin kept at dark redness. The reaction takes place with incandescence. The resulting mass is extracted with water. The presence of large doses of barium sulphate in the sulphide moderates advantageously the reaction by preventing the too rapid decomposition of the nitrate.

The Action of the Diamines upon the Diacetones.—M. Alphonse Combes.—This paper is not adapted for useful abstraction.

On Crystalline Tanghinine Extracted from the Tanghinia Venenifera of Madagascar.—M. Arnaud.—This poisonous principle is concentrated in the kernel of the fruit of an Apocyeous tree. The oily matter, which forms about 75 per cent of the kernel, is perfectly harmless. Tanghinine is a heart-poison, approximating to strophantine and ouabaïne, but, unlike these two, it has a general convulsive action. From 2·550 kilos. of the kernels the author obtains 25 grms. of pure crystalline tanghinine. It is colourless, and crystallises in rhombs from its alcoholic solution. It is anhydrous, and gives no coloured reactions. It melts at 182° to a transparent liquid, and if heated more strongly it burns without any residue. It is very sparingly soluble in water, moderately soluble in ether, and freely soluble in strong alcohol. It deflects the plane of polarised light to the left. If heated with dilute acids it is decomposed, yielding a yellowish resinous product. No reductive sugars are formed, such as are obtained from ouabaïne, strophantine, and the other glucosides. It contains rather more carbon than ouabaïne and strophantine, but like the two latter, no nitrogen. It is therefore neither an alkaloid nor a glucoside.

The Expansion of the Spectral Rays of the Metals.—M. Gouy.—(See p. 5).

Colloid Cellulose, Soluble and Insoluble; Constitution of Parchment Paper.—C. E. Guignet.—Dry cellulose in contact with sulphuric acid at 50° B., if the temperature is not allowed to rise, is converted into a transparent gelatinous mass. At 100°, or even below that point, it is quickly converted into dextrine. After being completely washed, colloid cellulose dissolves in pure water. The solution is precipitated by very small quantities of sulphuric or nitric acid, sodium chloride, or sulphate-lead acetate, &c. Vegetable parchment is a tissue of ordinary cellulose, the pores of which are filled up with colloid cellulose.

No. 25, June 24, 1889.

The Condition of Matter near its Critical Point.—L. Cailletet and E. Colardeau.—The authors conclude that the critical temperature of a liquefied gas is not that where the liquid evaporates totally and abruptly in the containing space. The liquid state persists beyond this temperature. Neither is it the temperature at which a liquid and its saturated vapour have the same density. It is the temperature at which a liquid and the gaseous atmosphere above it become capable of mutual solution in all proportions, forming, after ignition, a homogeneous mixture.

The Formation-Heat of the Hyponitrites.—M. Berthelot.—The author finds that the formation of hyponitrous acid takes place with a considerable absorption of heat.

The Occlusion of Gases in the Electrolysis of Copper Sulphate.—A. Soret.—Electrolytic copper contains only two gases, one of which, hydrogen, is generally

in excess, always, indeed, if the electrolyte is acid. The fragility of the deposits is correlated with the presence of carbonic acid in excess.

The Ammoniacal Compounds of Ruthenium.—A. Joly.—The salts of the ammoniacal ruthenium bases do not correspond to any of the salts of the ammoniacal bases of the other platinum metals. Jörgensen, who has made an elaborate study of the ammoniacal rhodium compounds, has indicated the relations of isomorphism, connecting them to the ammoniacal compounds of cobalt and chrome, discovered by Fremy. Here we can find nothing similar; at the utmost the ruthen-ammonium salts may be approximated to the fusco-cobaltic salts.

Researches on the Hyponitrites.—M. Maquenne.—The author describes the silver, barium, ethyl, calcium, and strontium hyponitrites, and the calcium, strontium, and barium acetohyponitrites. He concludes that nitrous oxide cannot be the anhydride of hyponitrous acid.

The Presence of Sodium Sulphate in the Atmosphere and the Origin of Saline Dust.—P. Marguerite-Delacharlonny.—The author considers that every soluble salt contained in waters and in the soil must be carried away by the evaporation of its solution, and must be found in small quantities in the air.

The Camphor and the Borneol of Rosemary. New Method of Separating Camphor and Borneol.—A. Haller.—The camphor of rosemary is a mixture of dextro-camphor and borneol, and of laevo-camphor and borneol. In order to separate camphor and borneol, the author triturates 200 grms. of the sample with about 120 grms. of pulverised succinic acid, and heats the mixture for forty-eight hours in flasks to about 140°. When the flasks are withdrawn from the oil-bath the contents separate into two layers: the one, solid and crystalline, consists of succinic acid; the other, a yellowish liquid, floats at the top, and contains a combination of succinic acid with borneol and also the camphor. The whole is then treated with ether, which dissolves the camphor and the acid borneol succinate, whilst the succinic acid remains insoluble. The ethereal liquid, after being repeatedly agitated with a solution of sodium carbonate, deposits the acid borneol succinate, whilst the camphor remains dissolved.

Zeitschrift fur Physikalische Chemie.
Vol. iii., Part 2.

Evaporation and Dissociation. The Continuous Transition from the Gasiform to the Liquid Condition at all Temperatures.—W. Ramsay and Sydney Young.—The substance of this memoir will be found in the *Philosophical Magazine* for 1887, p. 196.

Evaporation and Dissociation. A Study of the Thermic Properties of a Mixture of Ethylic Alcohol and Ether.—W. Ramsay and Sydney Young.—From the *Journal of the Chemical Society*, 1887, p. 755.

The Molecular Weight of Nitrogen Dioxide.—W. Ramsay.—According to the results of five experiments the molecular weight of this compound is 92, and its formula N_2O_4.

Remarks on H. Biltz's Memoir on the Molecular Magnitude of Sulphur.—W. Ramsay.—The author considers it not disproved that sulphur exists as S_6. Biltz's experiments merely give room to the conjecture that there may possibly exist more complicated molecules, such as S_8 or S_{10}.

The Absorption of Hydrogen by Metals.—Dr. Max Thoma.—The author's chief results are:—1. The increase of palladium in bulk, when charged electrolytically with hydrogen, takes place equally in all directions. 2. The contractions on discharge by the development of oxygen become smaller with the number of charges, but show no regularity. 3. Palladium can absorb permanently only a certain quantity of hydrogen. Any proportion of hydrogen taken up in excess is spontaneously liberated. 4. Below this limit of saturation the expansion of palladium and of the alloy of palladium and platinum are proportional to the quantities taken up. 5. The absorption of hydrogen by palladium and by the alloy above the limit of saturation, is attended with expansion, and its spontaneous elimination with contraction. 6. In palladium the expansion by supersaturation is equal to the contraction on the spontaneous escape of hydrogen. 7. To each strength of current there corresponds a certain degree of supersaturation which cannot be raised by protracted electrolysis. 8. Probably with the supersaturation, reached at any given strength of current, there occurs a stationary condition, in which as much hydrogen penetrates into the cathode per second as there is set free in the same time. 9. After the limit of saturation has been exceeded the volume of palladium increases more rapidly for an equal absorption of hydrogen than corresponds to a similar absorption below the limit. Hence in supersaturated palladium the hydrogen exists in a far lower density than it does in palladium below the limit of saturation. 10. Hydrogen diffuses itself in palladium wire in the course of half an hour to a distance of 4—5 m.m. from the point of the wire exposed to electrolysis. 11. In the supersaturated state both palladium and its platinum alloy show a far greater hydrogen polarisation than in the saturated state. 12. Iron, as well as palladium, can be supersaturated with hydrogen, so that the gas is spontaneously eliminated. 13. This supersaturation occurs when iron comes in contact with dissociated hydrogen in the voltameter or on the action of acid upon the iron, but not when the iron is exposed to free hydrogen. 14. In iron a certain degree of supersaturation corresponds to every strength of the current. 15. The quantities of hydrogen spontaneously evolved from supersaturated iron are proportional to the surfaces of the charged iron.

Isotonic Coefficients of Certain Salts.—Hugo de Vries.—The salts examined are urea, magnesium sulphate, potassium, lithium, ammonium, calcium, magnesium, and strontium chlorides, calcium nitrate, and potassium ferrocyanide.

A Simple Diffusion Experiment.—W. Beyerinck.—This paper requires the accompanying woodcut.

On Raoult's Law of the Depression of Freezing-Points.—J. F. Eykman.—The numbers found experimentally range around the theoretical value, so that the author considered further determinations superfluous.

Simple Derivation of Relation Between Osmotic Pressure and Depression of Vapour Tension.—S. Arrhenius.—This memoir requires the two accompanying woodcuts.

On Free Ions.—W. Ostwald and W. Nernst.—This memoir does not admit of brief reproduction.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Thiocamf.—(Reply to G. E. Wright)—The thiocamf disinfectant may be purchased from the Thiocamf Disinfectant Company, 5, Lower Merrion Street, Dublin.—E. A. Werner.

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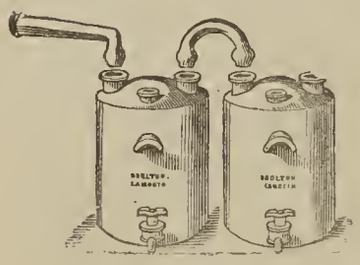

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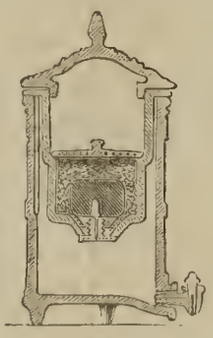

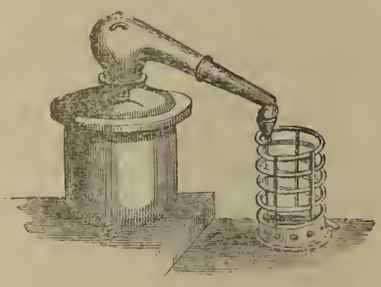

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July 12, 1889.

THE CHEMICAL NEWS.

Vol. LX. No. 1547.

ON RECENT RESEARCHES ON THE RARE EARTHS AS INTERPRETED BY THE SPECTROSCOPE.*

By WILLIAM CROOKES, F.R.S., &c.

If I name the Spectroscope as the most important scientific invention of the latter half of this century, I shall not fear to be accused of exaggeration. Photography has rendered vast services in recording astronomical and biological phenomena, and it even supplies us with indirect means of studying ray vibrations to which the human retina does not respond. The electro-acoustic devices of Edison and his co-workers permit almost magical communication between human beings. Ruhmkorff's coil and the Geissler tube have rendered notable service in physical investigation; and the electric lamp promises to aid in exploring the internal parts of living animals, as well as in studying the organic forms of the deep sea. But in the spectroscope we possess a power that enables us to peer into the very heart of Nature. In the extent of its grasp and the varied character of its applicability it surpasses the telescope and at least rivals the microscope. It enables the astronomer to defy immeasurable distance, and to study the physical condition and the chemical composition of the sun and the stars as if they were within touch, and even to ascertain the direction of their movements.

Without attempting to discuss the import of the results thus gained—which would lead us too far—I may point out that they overthrow a dogma concerning the classification of the sciences. It has been said that the simpler and more general sciences lend both doctrines and methods to the more complex and less general sciences, and that the latter give nothing in return. But we now see chemistry endowing astronomy with an original and fruitful method of research.

Turning to the very opposite extremity of the scientific hierarchy we find that to the biologist the spectroscope is of value in studying the relations of animal and vegetable fluids, and even of certain tissues. But this wonderful instrument is clearly destined to play its chief part in what is called terrestrial chemistry—the field where it has won the most signal triumphs.

It must be remarked, despite this vast range of applicability, a range sweeping through the whole universe and embracing all the four elements of antiquity; and despite the astonishing results already achieved and the prospect of greater revelations to come, that the spectroscope is still inadequately appreciated by professed men of science, and in consequence is, to a great extent, ignored by the "educated and intelligent public." In urging its more thorough recognition I do not advocate the formation of spectroscopic societies for the fragmentary study of everything that can be observed with a spectroscope. But I recommend researching chemists to appeal to this instrument wherever requisite and possible.

An elaborate spectroscopic study of the basic constituents of rare minerals from different localities would be of great value, and I would suggest that on all possible occasions meteorites should be submitted to careful spectroscopic analysis.

* Address delivered by the President of the Chemical Society at the Annual General Meeting March 21st, 1889.

I do not propose to discuss all the splendid achievements of the spectroscope in chemistry; nor its applications in ordinary analysis, qualitative and quantitative; nor the conduct of technical operations, such as the Bessemer process. I confine myself to the light thrown by the spectroscope upon the nature and the relations of our *elements*, real or supposed.

Though systematically employed by few experimentalists, the spectroscope has already led to the discovery of several hitherto unknown elements. In the early days of spectrum analysis attention was mainly concentrated on the flame spectra: that is, the bodies in question were vaporised and rendered luminous by the action of a flame, such as that of the Bunsen burner or of the oxyhydrogen jet. This procedure in the hands of Bunsen and Kirchhoff gave us cæsium and rubidium; afterwards, in my own hands, thallium; and in those of Reich and Richter, indium.

Then followed the production and examination of spark-spectra. The spark produced by means of the induction coil, especially when its energy is reinforced by the intercalation of a Leyden jar, volatilises and renders luminous minute portions of matter, solid, liquid, or gaseous, which may then be examined by the spectroscope. In this manner gallium was discovered in 1875 by Lecoq de Boisbaudran. In consequence of the sharpness and the well-marked character of these spark-spectra they are relied on by chemists as certain proof of the identity of any two elements which yield identical spectra.

Next was introduced the systematic study of the absorption-spectra seen when a beam of light is passed through certain transparent solids or through solutions of various substances. One of the earliest observers in this branch of spectroscopy was Dr. Gladstone, who, in 1858, read before this Society a paper on the absorption of light by various metallic salts, and gave the first description of the absorption-spectrum of didymium. This branch of spectroscopy has proved not less fruitful in the recognition of new metallic elements.

In the investigation of the rare earths my principal object has been to separate the true from the undemonstrated and spurious, verifying the true, rejecting the spurious, and reducing as far as possible the number of the doubtful. In the following table I have given a list of the so-called "rare-elements," with which for the last seven or eight years I have been specially occupied. Column 1 gives the names by which they are commonly known. Column 2 gives their atomic weights, &c. Column 3 shows in what manner they come under the domain of spectroscopy; and columns 4 and 5 notify the components or meta-elements into which some of these bodies have been decomposed in 1886 by myself, and in 1887 by Krüss and Nilson. In the first column I have exercised a judicial leniency in retaining candidates, for the sake possibly of old associations, when strict justice would have disestablished them. Thus, it may be doubted whether decipium, philippium, or gadolinium should have been retained. But since doubts have been cast on the integrity of nearly all the occupants of this column the line should not be drawn too strictly.

At first spectroscopic examination was applied directly to substances, natural or artificial, which had not undergone any special preparation. The idea next occurred of attempting to split up substances supposed to be simple into heterogeneous constituents before appealing to the spectroscope. The refined chemical processes used for this operation may be summarised under the name of fractionation, whether they be fractional precipitations, crystallisations, or decompositions. The essential principles of this processes were so fully discussed on the last occasion when I had the honour of addressing you that I need not further allude to them.

The Didymium Group.

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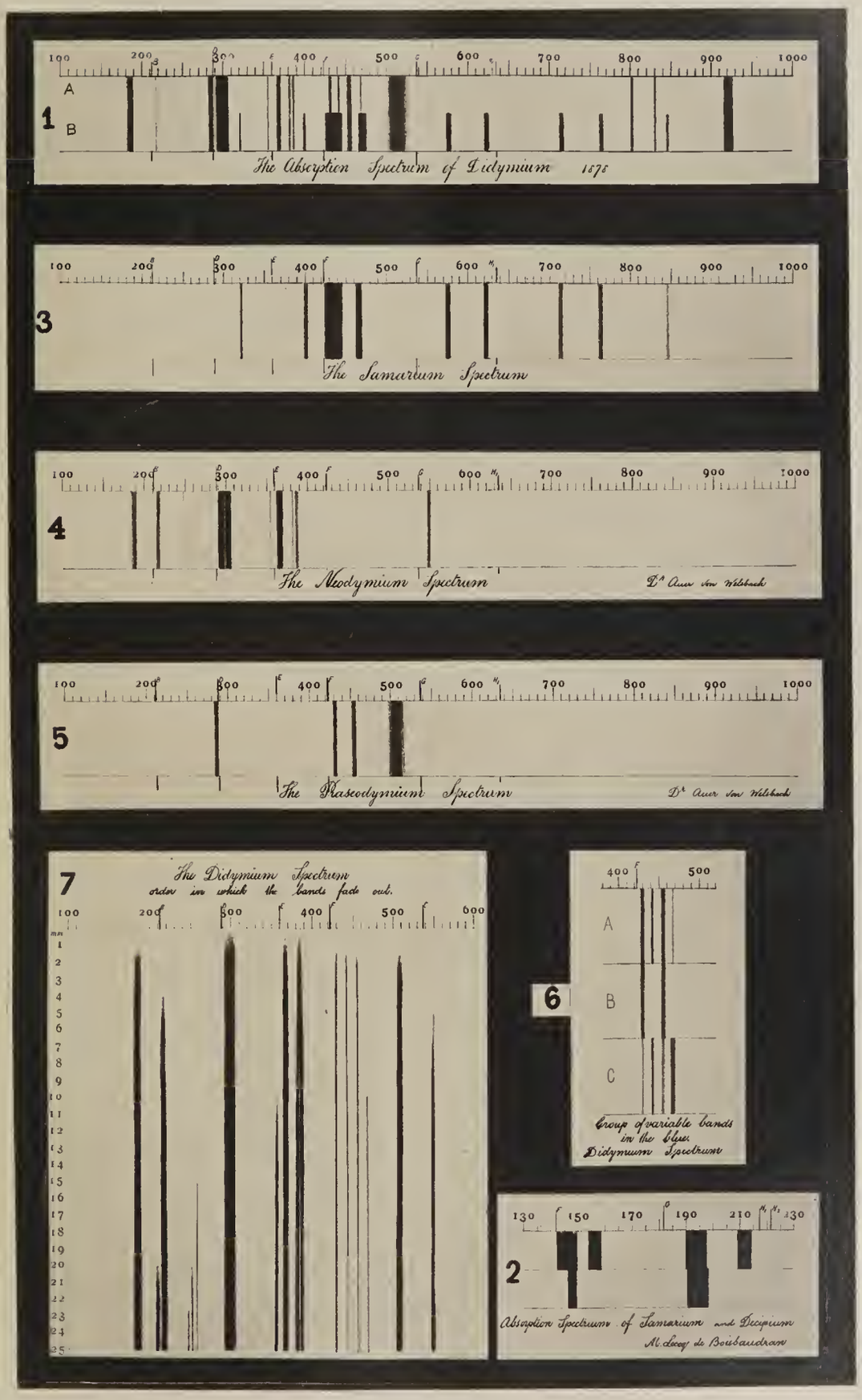
TABLE I.

	Atomic weight of Metal and Formula of Oxide.	Gives Spectrum by—	Component Meta-Elements according to— Crookes (1886).	Nilson and Krüss (1887).
Didymium ..	Neodymium— 140·3, Nd_2O_3. Praseodymium— 143·6, Pr_2O_3. Unnamed.	Absorption.	Dα, λ=475	Diα, Diβ, Diγ, Diδ, Diε, Diη, Diθ, Diι, Diχ
Decipium				
Samarium ..	150·12, Sm_2O_3.	Absorption and phosphorescence.	Sδ, Gε, Gγ, Gθ	Smα, Smβ
Lanthanum ..	138, La_2O_3.	Phosphorescence.		
Erbium	166, Er_2O_3.	Absorption, and phosphorescence.	λ 550, λ 493	Erα, Erβ
Philippium ..	45—48, PpO.	Phosphorescence.		
Holmium		Absorption.		Xα, Xβ, Xγ, Xδ
Thulium	170·7, Tm_2O_3.	Absorption.		Tmα, Tmβ
Dysprosium ..		Absorption.	λ 457—448 (1888)	Xζ, Xε, Xη
Yttrium	88·9, Yt_2O_3.	Phosphorescence.	Gα, Gβ, Gδ, Gζ, Gη	Zα, Tb, Yt (Lecoq de Boisbaudran.)
Terbium	124·7, Tb_2O_3.			
Gadolinium (Yα)		Phosphorescence.	Gβ, Gζ	
Ytterbium ..	173·01, Yb_2O_3.	Phosphorescence.		
Scandium ..	44·03, Sc_2O_3.			

processes with spectroscopic examination applied to bodies showing absorption spectra soon led to important discoveries. Fig. 1A* shows what I may call the normal didymium spectrum, as it was generally recognised down to the year 1878. Fig. 1B shows the whole of the absorption-bands belonging to bodies subsequently separated from didymium by fractionation. When in 1878 the didymium from samarskite was examined by Delafontaine (*Compt. Rend.*, lxxxvii., 632; CHEM. NEWS, xxxviii., 223) he found it to differ somewhat from ordinary didymium as extracted from cerite and gadolinite, and by a series of chemical fractionations he succeeded in separating from it an earth which he called decipium, giving at least three absorption-bands, one having a wave-length of 416 ($1/\lambda^2$ 578); another narrower and stronger, at wave-length 478 ($1/\lambda^2$ 438), and a very faint "minimum of transmission" near the limit of the blue and green. Nine months later Lecoq de Boisbaudran (*Compt. Rend.*, lxxxix., 212; CHEM. NEWS, xl., 99) announced the discovery of samarium as a constituent of the didymium from samarskite, giving a drawing of the decipium and samarium spectra to a common scale (Fig. 2), from which it is seen that samarium is characterised by the bands of Delafontaine's decipium together with two additional bands. Fig. 3 shows the samarium spectrum from the latest measurements.

Still didymium was not reduced to its ultimate simplicity. In 1885 Carl Auer (*Monatsh. Chem.*, vi., 477), by fractionally crystallising the mixed nitrates of ammonium, didymium, and lanthanum, showed it was thus possible to cleave didymium in a certain direction and separate it into two other bodies, one giving green salts and the other pink salts. Each of these has a characteristic absorption spectrum, the sum of the two sets of bands approximating to the old didymium spectrum. These bodies the discoverer has named respectively praseodymium and neodymium. The neodymium spectrum (Fig. 4), according to Auer, consists of the whole of the bands in the red, with part of the large one in the yellow; it then misses all the green and blue, and takes in the second line in the violet. Fig. 5 is the spectrum of praseodymium, which I have also taken from Auer's description;

* All the figures are drawn to the $1/\lambda^2$ scale.



SPECTROSCOPIC RESEARCHES ON THE RARE EARTHS.

W. CROOKES.

it takes the other part of the yellow band, and all the green and blue, except the second blue, which belongs to neodymium. Subtracting these two spectra from the old didymium spectrum (Fig. 1) you see there are still two bands left at λ 462 and 475 ($1/\lambda^2$ 465 and 443). Assuming that the argument from absorption-spectra is a legitimate one—and all recent research tends to show that if not quite trustworthy it is at all events a weighty one—the inference I draw from these results is that the old didymium still contains a third body distinct from neo- and praseodymium, to which one or both of these extra bands is due.

I must venture to lay especial emphasis on the words *in a certain direction*. Didymium in my own laboratory has undergone other cleavages, and I have not yet decided whether we shall have to recognise further decompositions of neodymium and praseodymium, or whether the original didymium is capable of being resolved differently according to the manner in which it is treated. Keeping the band in the orange always of the same strength, in many of the fractions of didymium from different sources the other bands of neo- and praseodymium are seen to vary from very strong almost to obliteration (Chem. News, liv., 27). In this way I have worked on the spectra of didymium from allanite, cerite, euxenite, fluocerite, gadolinite, hielmite, samarskite, yttrotitanite, &c., and the further I carry the examination the more the conclusion is forced upon me that didymium must not be regarded as compounded of two elements only, but rather as an aggregation of many closely allied bodies. Later researches of Krüss and Nilson have led them to the same conclusion.

When working in 1886 on the decomposition of the nitrate of didymium by heat, I found very decided indications of the possibility of depriving didymium of band after band until only the deep line in the blue λ 443 ($1/\lambda^2$ 509·6) is left (*Proc. Roy. Soc.*, xl., 503). I have provisionally named this single band element Dα. In this connection I would like to draw your attention to a few facts which have very recently come to light.

In some of my fractions of didymium the band λ 475 ($1/\lambda^2$ 443) intensifies in company with another band at λ 462 ($1/\lambda^2$ 465). Fig. 6 shows at A the group of blue bands as they are seen in a strong solution of didymium. It forms a well-marked set of four comparatively sharp lines, one at λ 462 ($1/\lambda^2$ 465) being the faintest. Under these lines I show (Fig. 6, B) the same group as seen in fractions of the same solution of didymium after disintegration has commenced. This fraction is very similar to Auer's praseodymium; and below this (Fig. 6, C) I again show the same group as seen in the didymium fractions most removed from the one last described. Here the two lines λ 475 ($1/\lambda^2$ 443) and λ 462 ($1/\lambda^2$ 465) have become very strong, while the other two have almost faded out. One of these, λ 475 ($1/\lambda^2$ 443), is included by Auer in the spectrum of his crude didymium, but he makes no further reference to it either in description or diagram. Of these lines, λ 462 ($1/\lambda^2$ 645), probably belongs to the samarium group, but the other, λ 475 ($1/\lambda^2$ 453), cannot belong to samarium, although it superposes on the most refrangible half of the broad and ill-defined samarium band.

In a paper read before the Royal Society dated June 9, 1886 (*Compt. Rend.*, cii., 1551), I gave an account of some observations I had made upon the line λ 475 ($1/\lambda^2$ 443), proving that it could be separated from the old didymium spectrum, and in conclusion said it "must be regarded as characteristic of a new body."

Subsequent to my paper Demarçay (*Ibid.*) drew attention to this line at λ 475 ($1/\lambda^2$ 443), and in 1887 (*Compt. Rend.*, civ., 580) he again returned to the subject, associating the two lines λ 475 ($1/\lambda^2$ 443) and λ 462 ($1/\lambda^2$ 465) as being due to the same element. With this opinion I cannot yet agree, for in many instances I have had fractions in which the relative intensities of the two are widely different. More recently Krüss and Nilson have ascribed this line to one of the constituents of Soret's X or holmium, which gives a line falling nearly on the same place (Chem. News, lvi., 154, 173).

By examining the absorption-spectra of solutions of rare earths obtained from widely different sources, Krüss and Nilson (*Ber.*, xx., Part xii., 2134; and Chem. News, lvi., 74, 85, 135, 145, 154, 165, 172) came to the conclusion that the elements giving absorption-spectra, and known as didymium, samarium, holmium, thulium, erbium, and dysprosium, were not homogeneous, but that each one contained almost as many separate components as it produced bands of absorption.

They have discovered that in didymium obtained from some minerals one of the fainter lines of the normal didymium spectrum is strong, while others usually stronger are almost or quite absent; results to which I shall presently refer will show that this cannot be explained by dilution or concentration. In this way, by examining a great number of minerals, they found anomalies occurred in the case of almost each of the old didymium lines, and therefore decided, as above mentioned, that it is a compound body, capable of resolution into at least nine separate components.

Identical arguments are brought forward to prove that each of the other so-called elements, samarium, erbium, holmium, thulium, dysprosium, &c., are compounds of many closely allied bodies.

Krüss and Nilson, I believe, are pushing their investigations with the object of isolating the separate components of these different earths. They, however, question the possibility of resolving the erbia and didymia earths into their several ultimate constituents by a fractionated decomposition of the nitrates. In fact they assert that by means of the methods of separation at present known it would be almost impossible to completely isolate any single constituent of the mixed earths. They therefore propose, as I had previously done,* a method by which we may certainly arrive nearer to the mark and dispense with much tedious fractionation. If we examine the minerals which contain these rare earths we find they occur in very different states of mixture or combination. Sometimes many of the constituents which we wish to separate are conjointly present, and sometimes but few. The desired differentiation, in fact, has already been commenced by Nature. Krüss and Nilson, therefore, whichever ingredient they wish to separate, propose to operate on a mineral which contains that ingredient as far as possible in a state of isolation. In other words, they will take advantage of the work that Nature has already begun, and endeavour by refined chemical means to put the last finishing touches to her work. Thus they will be able to work with smaller quantities of primary material,—no small consideration in the case of some minerals,—and to obtain results in a shorter time. How widely the composition of one and the same mineral, as judged by our searching physical tests, may vary, will be seem from the following instances. Fergusonite from Arendal shows six of the bands of holmium, fergusonite from Ytterby four, and that from Hitterö only three. Moreover, the ingredient provisionally called Xα is to be found in the fergusonite from Ytterby, but not in that of Arendal and Hitterö.

The foundation for thus firmly declaring what I had previously ventured to infer, is the striking differences in the spectra given by several specimens of one earth, say didymium, when obtained from different sources.

We are anxiously waiting the results of this investigation, but although the paper quoted was published in July, 1887, no further communication has come from these illustrious workers.

Chemists recently have stated as proof of the existence of new elements the fact that certain bands of absorption, as seen in various fractions, "follow the same variations of intensity." Before deciding the question whether

* "Address to the Chemical Section of the British Association, Birmingham Meeting," Chem. News, liv., 123. "On the Fractionation of Yttria," Chem. News, liv., 157. *Proc. Roy. Soc.*, xl., 1886. 505

didymium is a homogeneous whole, or whether an argument in favour of its heterogeneity can be based on the fact that the absorption spectra of didymium from different minerals differ *inter se*, it was necessary to ascertain if the absorption-bands seen in its solutions, whatever the thickness of the layer, whether dilute or concentrated, followed the same variations, and also to ascertain the nature of these variations. To contribute to this inquiry I examined the absorption-spectrum of a solution of neutral didymium nitrate containing one part by weight of metal in 10 of water, as seen through a series of cells from 1 m.m. to 25 m.m. in thickness. For this work I used a new form of binocular spectroscope, fitted with a mechanical tracing arrangement, so that each spectrum can be automatically mapped on paper strips; from this set of tracings I have arranged the diagram (Fig. 7) now before you. It represents the bands of the normal didymium spectrum. The figures running up the side represent the thickness of the layer of solution observed, and they show at a glance the "life" of each of the bands. At the bottom, 25 m.m. thickness, all the known bands are visible, and they become fainter and die out in the particular order here given, some of them remaining visible almost to the end. For instance, almost as long as the deep line in the blue part of the spectrum at λ 443 ($1/\lambda^2$ 509), my Dα, can be distinguished, it is possible to see the group of three very narrow ones next to it. Two or three other less characteristic bands can be seen only when there is a very considerable depth of liquid; thus, the three lines in the red λ 636, 628, 622 ($1/\lambda^2$ 247, 253, 258), cannot be seen distinctly through less than 20 m.m. of this strength of solution.

Having ascertained in this series how the spectra varied in appearance with different thicknesses of the same solution (strength 1 of Di in 10 of water), I repeated the experiments, keeping the thickness of layer of solution constant, and diluting the standard solution of didymium so that the rays of light passed through the same quantity of metal as in the former series. The results in each case were practically identical; the differences being too slight to be detected in my apparatus. The spectrum exhibited, for instance, by 1 m.m. of the standard solution of didymium is found to be identical with the spectrum shown by the same solution diluted 20 times and viewed through a 20 m.m. cell.

It will be seen that in the case of 1 m.m., not only the line in the yellow at λ 582 ($1/\lambda^2$ 292)* is to be seen, but also two in the green at λ 525 ($1/\lambda^2$ 368) and λ 510 ($1/\lambda^2$ 382). Therefore, to get a more simple spectrum, I diluted the solution to 1 of didymium in 20 of liquid. I m.m. thickness of this shows little else than a broad faint trace of the line in the yellow, λ 582 ($1/\lambda^2$ 292).

(To be continued).

AN ATTEMPT TO APPLY TO CHEMISTRY ONE OF THE PRINCIPLES OF NEWTON'S NATURAL PHILOSOPHY.†

By D. MENDELEEFF, LL.D.,
Professor of Chemistry in the University of St. Petersburg.

(Concluded from p. 17).

WHAT I have said appears to me sufficient to show that the principle of substitution adequately explains the composition, the isomerism, and all the diversity of combination of the hydrocarbons, and I shall limit the further development of these views to preparing a complete list of every possible hydrocarbon compound containing three atoms of carbon in the molecule. There are eight in al, of which only five are known at present.*

Among those possible for C_3H_6 there should be two isomers, propylene and trimethylene, and they are both already known. For C_3H_4 there should be three isomers: allylene and allene are known, but the third has not yet been discovered; and for C_3H_2 there should be two isomers, though neither of them are known as yet. Their composition and structure is easily deduced from ethane, ethylene, and acetylene, by methylation, methylenation, by acetylenation, and by carbonisation.

1. $C_3H_8 = CH_3CH_2CH_3$ out of CH_3CH_3 by methylation. This hydrocarbon is named propane.

2. $C_3H_6 = CH_3CHCH_2$ out of CH_3CH_3 by methylenation. This substance is propylene.

3. $C_3H_6 = CH_2CH_2CH_2$ out of CH_3CH_3 by methylenation. This substance is trimethylene.

4. $C_3H_4 = CH_3CCH$ out of CH_3CH_3 by acetylenation, or from CHCH by methylation. This hydrocarbon is named allylene.

5. $C_3H_4 = \begin{matrix}CH\\CH_2\end{matrix}CH$ out of CH_3CH_3 by acetylenation, or from CH_2CH_2 by methylenation, because—

$$\begin{matrix}CH_2CH\\CH\end{matrix} = \begin{matrix}CHCH\\CH_2\end{matrix}.$$

This body is as yet unknown.

6. $C_3H_4 = CH_2CCH_2$ out of CH_2CH_2 by methylenation. This hydrocarbon is named allene, or isoallylene.

7. $C_3H_2 = \begin{matrix}C\\\end{matrix}CHCH$ out of CH_3H_3 by symmetrical carbonisation, or out of CH_2CH_2 by acetylenation. This compound is unknown.

8. $C_3H_2 = \begin{matrix}CH_2\\\end{matrix}CC$ out of CH_3CH_3 by carbonisation, or out of CHCH by methylenation. This compound is unknown.

If we bear in mind that for each hydrocarbon serving as a type in the above tables there are a number of corresponding derivatives, and that every compound obtained may, by further methylation, methylenation, acetylenation, and carbonisation, produce new hydrocarbons, and these may be followed by a numerous suite of derivatives and an immense number of isomeric bodies, it is possible to understand the limitless number of carbon compounds, although they all have the one substance, methane, for their origin. The number of substances is so enormous that it is no longer a question of enlarging the possibilities of discovery, but rather of finding some means of testing them, analogous to the well-known two which for a long time have served as gauges for all carbon compounds.

I refer to the law of even numbers and to that of limits, the first enunciated by Gerhardt forty years ago, with respect to hydrocarbons, namely, that their molecules always contain an even number of atoms of hydrogen. But by the method which I have used of deriving all the hydrocarbons from methane, CH_4, this law may be deduced as a direct consequence of the principle of substitutions. Accordingly, in methylation, CH_3 takes the place of H, and therefore CH_2 is added. In methylenation the number of atoms of hydrogen remains unchanged, and at each acetylenation it is reduced by two and in carbonisation by four atoms, that is to say, an even number of atoms of hydrogen is always added or removed. And because the fundamental hydrocarbon, methane, CH_4, contains an even number of atoms of hydrogen, therefore all its derivative hydrocarbons will also contain even numbers of hydrogen, and this constitutes the law of even numbered parts.

The principle of substitutions explains with equal simplicity the conception of limiting compositions of hydrocarbons, C_nH_{2n+2}, which I derived, in 1861,† in an

* The λ and $1/\lambda^2$ lengths given here are only approximate.

† A Lecture delivered at the Royal Institution of Great Britain, May 31, 1889.

* Conceding variable atomicity, the structurists must expect an incomparably larger number of isomers, and they cannot now decline to acknowledge the change of atomicity, were it only for the examples $HgCl$ and $HgCl_2$, CO and CO_2, PCl_3 and PCl_5.

† "Essai d'une théorie sur les limites des combinaisons organiques," par D. Mendeleeff, 2/11 aout 1861, *Bulletin de l'Académie i. d. Sc. de St. Petersbourg*, t. v.

empirical manner from accumulated materials available at that time, and on the basis of the limits to combinations worked out by Dr. Frankland for other elements.

Of all the various substitutions the highest proportion of hydrogen is yielded by methylation, because in that operation alone does the quantity of hydrogen increase; therefore, taking methane as a point of departure, if we imagine methylation effected $(n-1)$ times we obtain hydrocarbon compounds containing the highest quantities of hydrogen. It is evident that they will contain—

$$CH_4+(n-1)CH_2, \text{ or } C_nH_{2n+2},$$

because methylation leads to the addition of CH_2 to the compound.

It will thus be seen that by the principle of substitution —that is to say, by the third law of Newton—we are able to deduce, in the simplest manner, not only the individual composition, the isomerism, and relations of substances, but also the general laws which govern their most complex combinations, without having recourse either to statical constructions, to the definition of atomicities, to the exclusion of free affinities, or to the recognition of those single, double, or treble ties which are so indispensable to structurists in the explanation of the composition and construction of hydrocarbon compounds. And yet, by the application of the dynamic principles of Newton, we can attain to that chief and fundamental object—the comprehension of isomerism in hydrocarbon compounds, and the forecasting of the existence of combinations as yet unknown, by which the edifice raised by structural teaching is strengthened and supported. Besides, and I count this for a circumstance of special importance, the process which I advocate will make no difference in those special cases which have been already so well worked out, such as, for example, the isomerism of the hydrocarbons and alcohols, even to the extent of not interfering with the nomenclature which has been adopted, and the structural system will retain all the glory of having worked up, in a thoroughly scientific manner, the store of information which Gerhardt had accumulated about the middle of the fifties, and the still higher glory of establishing the rational synthesis of organic substances. Nothing will be lost to the structural doctrine, except its statical origin; and as soon as it will embrace the dynamic principles of Newton, and suffer itself to be guided by them, I believe that we shall attain, for chemistry, that unity of principle which is now wanting. Many an adept will be attracted to that brilliant and fascinating enterprise, the penetration into the unseen world of the kinetic relations of atoms, to the study of which the last twenty-five years have contributed so much labour and such high inventive faculties.

D'Alembert found in mechanics, that if inertia be taken to represent force, dynamic equations may be applied to statical questions, which are thereby rendered more simple, and more easily understood.

The structural doctrine in chemistry has unconsciously followed the same course, and therefore its terms are easily adopted; they may retain their present forms provided that a truly dynamical, that is to say Newtonian, meaning be ascribed to them.

Before finishing my task and demonstrating the possibility of adapting structural doctrines to the dynamics of Newton, I consider it indispensable to touch on one question which naturally arises, and which I have heard discussed more than once. If bromine, the atom of which is eighty times heavier than that of hydrogen, takes the place of hydrogen, it would seem that the whole system of dynamic equilibrium must be destroyed.

Without entering into the minute analysis of this question, I think it will be sufficient to examine it by the light of two well-known phenomena, one of which will be found in the department of chemistry, and the other in that of celestial mechanics, and both will serve to demonstrate the existence of that unity in the plan of creation which is a consequence of the Newtonian doctrines. Experiments demonstrate that when a heavy element is substituted for a light one, in a chemical compound—an atom of magnesium in the oxide of that metal, for example, for mercury, the atom of which is $8\frac{1}{3}$ times heavier—the chief chemical characteristics or properties are generally, though not always, preserved.

The substitution of silver for hydrogen, than which it is 108 times heavier, does not affect all the properties of the substance, though it does some. Therefore chemical substitutions of this kind, the substitution of light for heavy atoms, need not necessarily entail changes in the original equilibrium; and this point is still further elucidated by the consideration that the periodic law indicates the degree of influence of an increment of weight in the atom as affecting the possible equilibria, and also what degree of increase in the weight of the atoms reproduces some, though not all, the properties of the substance.

This tendency to repetition, these periods, may be likened to those annual or diurnal periods with which we are so familiar on the earth. Days and years follow each other: but, as they do so, many things change; and in like manner chemical evolutions, changes in the masses of the elements, permit of much remaining undisturbed, though many properties undergo alteration. The system is maintained according to the laws of conservation in nature, but the motions are altered in consequence of the change of parts.

Next, let us take an astronomical case, such, for example, as the earth and the moon, and let us imagine that the mass of the latter is constantly increasing. The question is, what will then occur? The path of the moon in space is a wave-line similar to that which geometricians have named epicycloidal, or the locus of a point in a circle rolling round another circle. But, in consequence of the influence of the moon, it is evident that the path of the earth itself cannot be a geometric ellipse, even supposing the sun to be immovably fixed; it must be an epicycloidal curve, though not very far removed from the true ellipse, that is to say, it will be impressed with but faint undulations. It is only the common centre of gravity of the earth and the moon which describes a true ellipse round the sun. If the moon were to increase, the relative undulations of the earth's path would increase in amplitude, those of the moon would also change, and when the mass of the moon had increased to an equality with that of the earth, the path would consist of epicycloidal curves crossing each other, and having opposite phases. But a similar relation exists between the sun and the earth, because the former is also moving in space. We may apply these views to the world of atoms, and suppose that, in their movements, when heavy ones take the place of those that are lighter, similar changes take place, provided that the system or the molecule is preserved throughout the change.

It seems probable that in the heavenly systems, during incalculable astronomical periods changes have taken place, and are still going on, similar to those which pass rapidly before our eyes during the chemical reaction of molecules and the progress of molecular mechanics, may —we hope will—in course of time, permit us to explain those changes in the stellar world which have more than once been noticed by astronomers, and which are now so carefully studied. A coming Newton will discover the laws of these changes. Those laws, when applied to chemistry, may exhibit peculiarities, but these will certainly be mere variations on the grand harmonious theme which reigns in nature. The discovery of the laws which produce this harmony in chemical evolutions will only be possible, it seems to me, under the banner of Newtonian dynamics which has so long waved over the domains of mechanics, astronomy, and physics. In calling chemists to take their stand under its peaceful and catholic shadow I imagine that I am aiding in establishing that scientific union which the managers of the Royal Institution wish to effect, who have shown their desire to do so

by the flattering invitation which has given me—a Russian—the opportunity of laying before the countrymen of Newton an attempt to apply to chemistry one of his immortal principles.

ZIRCONIUM AND ITS ATOMIC WEIGHT.*

By G. H. BAILEY, D.Sc., Ph.D., The Owens College.

(Concluded from p. 18).

The Atomic Weight of Zirconium.

After what has been said it may appear that the previous determinations of atomic weight from the sulphate would be too high rather than too low, since there can be little doubt that Berzelius heated the salt above 400°. It does not follow, however, that by heating it for a short time at a moderately high temperature more than a small fraction of the salt would be brought under conditions favourable to decomposition, nor even would the temperature of the mass be such that the whole of the free sulphuric acid would be got rid of. And the fact that on repeating such a treatment no variation in weight occurred, would be no guarantee that the salt was normal zirconium sulphate. My own experiments show that to get rid of the excess of acid requires prolonged heating, and at the same time renewal of the atmosphere in the vessel containing the sulphate. Apropos of this, Berzelius's precaution to introduce into the crucible in the last stage of the ignition of the sulphate a little ammonium carbonate is a very necessary one, as it displaces often two or three m.grms. of sulphuric acid, which otherwise seems to remain in the crucible time after time and fix itself in the zirconia, when the crucible begins to cool. Furthermore, whatever previous experience may have been (for no special precaution is mentioned in any case), I have found it most difficult to ignite zirconium sulphate without loss ; the decomposition occurs with such violence at first, and the resulting zirconia is so extremely light, that, though every care was taken, varying results were got, even in igniting very gently over the Bunsen burner, some as low as 43 per cent of oxide instead of 43·3 at least. On carefully watching it was seen that minute particles of zirconia were being carried out of the crucible, although the cover fitted well. This loss was only avoided by enclosing the crucible within a second larger one, whose cover fitted quite closely and only communicated with the external atmosphere by a drawn-out neck, so that there were no air-currents. Even then, if the crucible was placed over the blowpipe flame at once, loss occurred, and it was necessary in every case to commence the operation over the flame of a Bunsen burner, and then after half an hour to transfer to the blowpipe.

Part of the determinations was made by Berzelius in the best way—that is, the zirconia was first precipitated by means of ammonia, and then the sulphuric acid determined in the filtrate by precipitation with barium chloride.

Having satisfied myself by careful comparative experiments that the results of both methods, under favourable conditions, correspond, I decided to adopt the dry method, viz., that of conversion of the sulphate into the oxide by ignition—

(*a*). Because it involved the least complicated operations and the fewest assumptions.

(*b*). Because under some circumstances basic zirconium sulphate is thrown down when ammonia is added to a solution of the sulphate.

In the following paragraphs are given the determinations of Berzelius and Mats Weibull from the sulphate, followed by those based upon my own experiments.

* A Paper read before the Royal Society, May 9, 1889.

Berzelius's Determination (*Pogg. Ann.*, vol. iv., p. 126).

From the analysis of the sulphate :—

SO_3	: ZrO_2 ::	100	: 75·84
,,	,,		: 75·92
,,	,,		: 75·80
,,	,,		: 75·74
,,	,,		: 75·97
,,	,,		: 75·85
Mean			75·853

$ZrO_2 : 2SO_3 :: 1·5171 : 2$
Zr : O :: 5·591 : 1
Zr : H :: 89·23 : 1

Mats Weibull's Determinations.

$Zr(SO_4)_2$.	ZrO_2.	$\frac{ZrO_2}{Zr(SO_4)_2}$.
1·5499 grms.	0·6684 grm.	43·126 per cent
1·5445 ,,	0·6665 ,,	43·153 ,,
2·1683 ,,	0·9360 ,,	43·168 ,,
1·0840 ,,	0·4670 ,,	43·081 ,,
0·7913 ,,	0·3422 ,,	43·321 ,,
0·6251 ,,	0·2695 ,,	43·113 ,,
0·4704 ,,	0·2027 ,,	43·091 ,,
Total 8·2335 grms.	3·5523 grms.	43·146 per cent

Mean determination :—

Zr : O :: 5·592 : 1
Zr : H :: 89·255 : 1

My Own Determinations.

$Zr(SO_4)_2$.	ZrO_2.	$\frac{ZrO_2}{Zr(SO_4)_2}$.
Portion A.		
2·62357 grms.	0·87785 grm.	43·381 per cent
2·6185 ,,	1·1354 ,,	43·360 ,,
Portion B.		
2·27709 grms.	0·08713 grm.	43·350 per cent
2·21645 ,,	0·96152 ,,	43·385 ,,
Portion C.		
1·75358 grms.	0·76107 grm.	43·4016 per cent
1·64065 ,,	0·7120 ,,	43·397 ,,
Portion D.		
2·33255 grms.	1·01143 grms.	43·361 per cent
1·81105 ,,	0·78485 ,,	43·337 ,,
Tot. 16·67344 grms.	7·23125 grms.	43·37 per cent

Maximum	Zr : O ::	5·674 : 1
	Zr : H ::	90·559 : 1
Minimum	Zr : O ::	5·654 : 1
	Zr : H ::	90·237 : 1
Mean	Zr : O ::	5·664 : 1
	Zr : H ::	20·401 : 1

Corrections in the Weighings.

The balance used could be read directly to $1\frac{1}{10}$ m.grms., and had been proved to be a most reliable instrument. The weights were an excellent set by Standinger, of Giessen, and showed an average variation from the normal amounting to only 0·000035 grm.

Corrections were introduced—

(*a*). For the weights.

(*b*). For displacement of air, and variations in temperature and pressure.

(*c*). For variations arising by reason of the different hygroscopic conditions of the desiccator and balance case.

In any case where condensation of moisture was liable to occur this was corrected for by noting the increment of weight per minute for several minutes whilst exposed in the balance case, and then constructing a curve with increment of weight and time as ordinate and abscissa,

from which the necessary correction at the time of weighing could be introduced. In nearly all cases over two grms. of the sulphate was used for each determination, and even with two grms. a difference of one m.grm. in the weight of the zirconia obtained implies a difference of 0·25 in the atomic weight; it is, therefore, evident that in some previous determinations where less than a grm. has been taken, there is considerable risk of error in the atomic weight.

THE ANALYSIS OF GLASSES.

By DAVID LINDO.

(Continued from p. 4).

The Ammonia Precipitate.

The filtrates and condensed washings from the silica having been united and set aside in a 200 c.c. flask, the greater portion of the liquid was poured into a beaker of the best hard Bohemian glass, concentrated, and ammonia was cautiously added to the hot liquid until the precipitate formed remained permanent on stirring. This precipitate was dissolved by adding the remainder of the acid liquid in the flask. The whole was then returned to the flask and sulphuretted hydrogen was passed in for fifteen to twenty minutes. The trace of sulphur precipitated was coloured from the presence of a trace of platinum, and sometimes lead. It was kept in closed flasks for two or three days, filtered through Gooch's, transferred to beaker, and concentrated. There was generally a slight cloudiness, which disappeared on further concentration; a few drops of nitric acid were added and the heating continued for some time. It was then precipitated carefully with ammonia in very slight excess, let stand for some time, and then filtered into the 200 c.c. flask, washed well with hot water, the washings concentrated in a platinum dish, and added to contents of flask, a little ammonia and ammonium sulphide added, and flask filled up to mark when cold. This portion serves for the estimation of lime and magnesia and last trace of silica.

The ammonia precipitate will contain much silica, ferric oxide, alumina if present, and also phosphoric acid in small quantity may be here, with possibly a trace of lime. It may be dealt with in a variety of ways.

First Method.—Dried on filter on sand-bath, transferred to crucible, ignited strongly, and weighed with the filter-ash, crushed with glass rod, fused with a little potassium bisulphate, boiled out with HCl and water, transferred to platinum capsule, evaporated to dryness, separated silica, and weighed in a small Gooch; added 1 grm. citric acid to filtrate, and then ammonia in very slight excess and acetic acid in slight excess. Tested with oxalate for lime. If none (or to filtrate if lime is present), added 30 c.c. magnesia mixture and ammonia, stirring well. If phosphoric acid precipitated it was filtered out and weighed. To the liquid or filtrate there was then added in a 100 c.c. stoppered flask ammonium sulphate to precipitate iron. After a day or two the iron sulphide is filtered, washed with water containing ammonium sulphide, dropped strong nitric acid upon filter, washed, evaporated to dryness on sand-bath, added a few drops nitric acid, and evaporated to dryness again two or three times. Ignited gently, dissolved in *aqua regia*, precipitated with ammonia in heat, filtered through small Gooch, ignited, and weighed as ferric oxide. The alumina is found by difference.

Second Method.—Ignited strongly and weighed. Transferred with ash of filter to a small steel mortar, crushed, ground fine in a small agate mortar, and fused in a platinum crucible with 5 or 6 grms. of the alkaline mixture, using a part to rinse the mortar. Conducted the fusion as usual, using 5 c.c. or more HCl to separate silica. The filtrate was nearly neutralised with ammonia and ammonium oxalate was added. Lime, if present, was filtered off. To the filtrate 1 grm. citric acid was added and ammonia in excess and 30 c.c. of magnesia mixture. The filtrate (or, if no phosphoric acid is present, the liquid) is treated as in method No. 1 to separate and determine iron. Alumina is found by difference.

Third Method.—In the absence of phosphoric acid in appreciable quantity the precipitate is dried on the sand-bath, but not ignited, and the total weight is not taken. The matter is crushed in a steel mortar, the filter is burnt, and the ash added to the precipitate and evaporated with HCl in a flat dish to separate silica. The concentrated filtrate is added to a solution of soda in a flat dish, heated, and the ferric oxide is separated through a small Gooch, and weighed. The filtrate is mixed in a small beaker with excess of HCl, and a little potassium chlorate is added, heated for some time, the alumina is precipitated with ammonia, collected in Gooch, washed, and weighed. The determination of the alumina in this method is direct. With most samples of glass, the quantities of lime being moderate, the trace carried down in the ammonia precipitate may be disregarded.

Fourth Method.—Dissolved the precipitate (after washing) with hot HCl, rather dilute, on the filter, washed the filter, and if it seemed that any silica had been separated out and retained by the filter, the latter is burnt and the ash added to the filtrate. This is then evaporated to dryness to separate silica, and its filtrate is treated as in method No. 3 to separate and determine iron and alumina directly. This method, like No. 3, is applicable only in the absence of appreciable quantities of phosphoric acid.

When precipitating with ammonia add the latter very cautiously to the hot liquid in very slight excess, and let stand a little before filtering. Avoid boiling, as it seems to render the precipitate less easily soluble in HCl.

In the absence of phosphoric acid, method No. 4 is better than No. 3. In presence of phosphoric acid method No. 2 is better than No. 1.

No. 3.— Three-quarter inch test-tubes going cloudy. Contains ferric oxide, 0·22 per cent; alumina, 1·11 per cent.

No. 10.—One inch test-tubes not cloudy. Ferric oxide, 0·3 per cent; alumina 2·01 per cent.

No. 29.—500 septem. flask, quite clear. Ferric oxide, 0·36 per cent; alumina, 2 per cent.

No. 34 A.—French glass tubing, not cloudy. Ferric oxide, 0·42 per cent; alumina, 2·29 per cent.

No. 34 B.—Ferric oxide, 0·14 per cent; alumina, 2·40 per cent. Neither of these determinations are trustworthy, the iron being too low and alumina too high.

No. 28.—A 300 c.c. cloudy flask. Ferric oxide, 0·29 per cent; phosphoric acid, 0·14 per cent. No alumina.

No. 22.—Cloudy pint tumbler. Ferric oxide, 0·3 per cent. No alumina.

No. 8.—Cloudy pipette. Ferric oxide, 0·27; alumina, 2·37.

A special test was applied to 5 grms. of the glasses in powder. It was mixed with 2 grms. ammonium fluoride in a flat dish, 3 c.c. pure sulphuric acid were added, and the dish was heated on the sand-bath and then over the lamp to expel most of the sulphuric acid. It was then boiled with dilute nitric acid, filtered, made up to 20 c.c., transferred to a small beaker, added 10 c.c. citric solution and ammonium nitrate and 10 c.c. molybdenum reagent, heated gently, and let stand. Most samples, if not all, contain a trace, at least, of phosphoric acid, as proved by this test. It is, however, in general, too small to interfere with the accuracy of the determinations if disregarded. It can only affect the determination of alumina in the second decimal. If more is present it must be separated.

No. 1.—Clear flask; reacts strongly. Ferric oxide, 0·21 per cent; alumina, 2·48 per cent.

No. 31.—Retort, quite clear, reacts slightly. Ferric oxide, 0·19 per cent; alumina, 0·82 per cent.

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JUNE 30TH, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, July 6th, 1889.

SIR,—We submit herewith the results of our analyses of the 168 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from June 1st to June 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 168 samples examined, six were recorded as "very slightly turbid." The remaining 162 samples were found to be clean, bright, and well filtered.

During the past month the progressive increase in degree of freedom from organic matter, manifested by the water supply during the first five months of the year successively, was not found to be sustained, but there was, on the contrary, a retrogression to about the degree recorded as prevailing a month or two back. Thus, taking the Thames-derived water for comparison, the mean proportion of organic carbon present in 100,000 parts of the water, during each of the first six months of the year respectively, was found to be as set forth below,—the mean proportion of 0·144 grain of organic carbon observed during the month of May, corresponding as nearly as may be to about a quarter of a grain of organic matter per gallon:—

Parts of Organic Carbon in 100,000 *Parts of Water.*

January	0·170	April	0·154
February	0·161	May	0·144
March	0·161	June	0·157

A like appreciable, though not important, retrogression was observable in respect of the degree of colour-tint of the water, and of the amount of oxygen required to oxidise the organic matter present; and was noticeable alike in the supply furnished by all the Companies, whether taking their supply from the Thames or the Lea.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

On Free Fatty Acids in Oils.—Hugo Noerdlinger.—The author dissolves the oils in a mixture of ether and alcohol (previously neutralised), adds phenolphthalein, and titrates with decinormal potassa. The proportion of free acid in vegetable oils is considerably greater than it has been generally supposed, and fluctuates between very wide limits, being affected by the ripeness of the plants, by climate, exposure, and weather, &c.—*Zeitschrift f. Anal. Chemie*, Part 2.

ON ALLOTROPIC FORMS OF SILVER.*

By M. CAREY LEA, Philadelphia.

SILVER is capable of existing in allotropic forms posessing qualities differing greatly from those of normal silver. There are three such forms, or rather three modifications of one form, differing from each other in many respects, but all more nearly related to each other than any one of them to normal silver. One of these forms is soluble in water, passing readily to an insoluble form, and this last may, by the simple presence of a neutral substance exercising no chemical action upon it, recover its solubility. Another form closely resembles gold in colour and lustre.

Whether metallic silver shall be reduced from its compounds in its normal or in an allotropic form, depends upon the reducing agent applied, so that it cannot be said with any certainty whether it exists in its compounds in its ordinary normal form or in an allotropic condition: the latter alternative seems at least equally probable.

These allotropic forms of silver are broadly distinguished from normal silver by colour, by properties, and by chemical reactions. They not improbably represent a more active condition of silver, of which common or normal silver may be a polymerised form. Something analogous has already been observed with other metals, lead, and copper.

Much having been written, especially within the last few years, on the products of the reduction of silver compounds, a brief summary of what has appeared may be desirable before proceeding further. The study of this subject has led to remarkable divergencies of opinion on the part of the chemists engaged in it. Almost all the views advanced have been successively disproved by each subsequent publication. It follows that what has obtained a place in the text-books is almost wholly incorrect.

The earliest experimental work was Faraday's, but his product has been proved to be a mixture.† The next was the well-known paper of Wöhler, published in 1839. It is not my purpose here to enter upon a criticism of this memoir. If this illustrious chemist succeeded in obtaining by the means employed a true citrate of silver hemioxide,—as would appear from his analyses—no chemist since his time seems to have done so. The next publication to Wöhler's was that of Von Bibra, who used Wöhler's method and, whilst affirming that he obtained a similar citrate, found an entirely different constitution for the corresponding chloride; for, instead of obtaining a hemichloride Ag_2Cl, he gives, as the result of fifteen concordant analyses, the constitution of his product as Ag_4Cl_3.‡ A citrate, to yield such a chloride (if such a chloride exists) by the simple action of hydrochloric acid, could scarcely have the constitution assigned to it by both Wöhler and V. Bibra.

In 1882 Pillitz published two papers.§ He commences by disputing the probability of the existence of Ag_4O on grounds of valency; namely, as implying that oxygen may be quadrivalent. Although it is very doubtful that any one has up to the present time obtained Ag_4O, the argument seems futile, as are many arguments deduced from supposed laws of valency. Similar reasoning would make Ag_2Cl impossible, which substance undoubtedly exists, and it would also deny the existence of K_2Cl, which stands upon such authority as that of Rose, Kirchhoff, and Bunsen.‖ Pillitz carefully examined the so-called hemioxide precipitated by alkaline solutions of

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* *American Chemical Journal*, Vol. xxxvii., No. 222.

† G. H. Bailey and G. J. Foster, *Chem. Soc.*, 1887, 416. *Berichte D. Ch. G.*, xx., Ref. 360.

‡ Bromann, *J. Prakt. Chim.*, 1875, 120, 39. Von Bibra precedes his paper with a brief summary of the conclusions reached by previous chemists on the subject of the action of light and chemical reducing agents on silver compounds. The collection is interesting, as showing to what inconsistent and even contrary opinions careful observers have come on these reactions.

§ *Zeitschrift fur Ann. Chemie*, xxi., p. 27, p. 496.

‖ "Gmelin Kraut," ii., 1, 72.

antimony and tin, and could find no trace of Ag_4O in any of them. He did not examine Wöhler's products.

The first person to deny categorically the existence of Wöhler's series of hemi-compounds of silver appears to have been Dr. Spencer Newbury. In two interesting papers* he describes a repetition of Wöhler's methods, and declares it to be impossible to obtain products of constant composition. The red solution taken by Wöhler to be argentous citrate, Dr. Newbury concludes to be a suspension of finely divided† silver. Muthmann, after a careful examination of Rautenberg's products, concludes that that chemist was wholly in error in asserting the formation of compounds of chromic, molybdic, and tungstic acids with silver hemioxide. He next studies the red liquid obtained by Wöhler's process, and comes to the same conclusion as Newbury : that it consists of finely divided silver suspended in water.

I shall not dispute the correctness of this opinion in the case of the liquid examined by these two chemists. At the same time I cannot accept the tests of solution employed by Muthmann. That a substance will not pass through a dialyser shows that it is colloidal, and is no proof whatever that it is not in solution. Animal charcoal takes up many substances from true solutions. Decolourisation by animal charcoal is no proof whatever that the colour removed was not in true solution. By freezing, the molecular condition of a substance may be changed. Muthmann found that when the red liquid was mixed with gum-water and precipitated by alcohol, the precipitated gum carried down with it the red substance, thence deducing that it was only in suspension. This conclusion is scarcely justified. A solution of litmus was mixed with gum-water and precipitated with alcohol ; the mass of the litmus went down with the gum, a trace only appeared in the filtrate. With Hoffmann's violet, the same result. Yet no one, I think, will assert that these two substances do not make true solutions in water. Even, however, if these arguments could be admitted they would not apply to the solutions presently to be described, which can be proved by optical means to be true solutions. I propose presently to show that silver may exist in a perfectly soluble form, dissolving easily and abundantly in water. Starting from this it may show all degrees of solubility down to absolute insolubility, still, however, existing in an allotropic form, and quite distinct from normal or ordinary silver. The solutions formed are as perfect as those of any other soluble substance.

Wöhler's process was next repeated by G. H. Bailey and G. J. Foster, who came to the conclusion that no citrate of hemioxide was formed, and that Wöhler's results must be rejected.

Von der Pfordten‡ endeavoured to obtain hemi-compounds of silver by acting on the nitrate with an alkaline solution of sodium tartrate, and also with phosphorous acid. His determinations were made volumetrically, based on an opinion that a permanganate solution acidified with sulphuric acid would dissolve silver hemioxide, but not metallic silver. Previously to receiving his paper I had found that sulphuric acid, even diluted with ten times its bulk of water, was capable of acting on finely divided normal silver, and of dissolving an easily recognised quantity. V. d. Pfordten's conclusions were thus vitiated entirely. It should, however, be remarked that the difficulties of the subject are extremely great. In his last paper§ this chemist abandons his views as to the existence of silver hemioxide ; so that at the present time the formation of Ag_4O by Wöhler's method, or by any other known method, is admitted by no one. That such an oxide may exist appears by no means improbable. The existence of Ag_2Cl and K_2Cl seems almost to involve that of Ag_4O and K_4O. This latter product Davy believed that he had obtained. The black substance which V. d. Pfordten formerly regarded as Ag_4O he now takes to be silver hydrate, Ag_4H_2O.

The reduction products described by V. d. Pfordten are strongly distinguished from those which I shall presently describe by two decisive reactions :—

1. None of his products could be amalgamated with mercury (l. c., 2296). All of mine readily amalgamate.

2. None of my products give off the slightest trace of gas when treated with dilute sulphuric acid. All of his do so (l. c., 2291).

Moreover, the difference of appearance is extremely great.

Early in the year 1886 I took up the study of the reduction products of silver in connection with that of the photo-salts. I commenced with Wöhler's process, giving it up after a few trials as affording no satisfactory results, and sought for a more reliable means. This I found in March, 1886, in a reaction which I still use : namely, the reduction of silver citrate by ferrous citrate. At first, however, the results obtained were most enigmatical, the products very unstable, and impossible to purify. Much time was lost, and the matter was given up more than once as impracticable. Eventually, by great modifications in the proportions, stable products and capable of a fair amount of purification were got. Even the earlier and less pure forms were exceedingly beautiful ; the purer are hardly surpassed by any known chemical products.

The forms of allotropic silver which I have obtained may be classified as follows :—

a. Soluble, deep red in solution, mat lilac, blue, or green whilst moist, brilliant bluish green metallic when dry.

b. Insoluble, derived from *a*, dark reddish brown while moist ; when dry, somewhat resembling *a*.

c. Gold silver, dark bronze whilst wet ; when dry, exactly resembling metallic gold in burnished lumps. Of this form there is a variety which is copper-coloured. Insoluble in water, appears to have no corresponding soluble form.

Properties Possessed by all the Varieties in Common, and Distinguishing them all from Normal Silver.

All these forms have several remarkable properties in common.

1. *That of Drying with their Particles in Optical Contact, and consequently Forming a Continuous Film.*—If either is taken in a pasty condition and is spread evenly over paper with a fine brush, it takes on spontaneously in drying a lustre as high as that of metallic leaf. C, when so treated, would be taken for gold leaf. But this property is much better seen by brushing the pasty substance over glass. When dry, an absolutely perfect mirror is obtained. The particles next the glass, seen through the glass, are as perfectly continuous as those of a mercurial amalgam, and the mirror is as good. A and B form bluish green mirrors, C gold or copper-coloured mirrors.

2. *The Halogen Reaction.*—When any of these allotropic forms of silver are brushed over paper, and the resulting metallic films are exposed to the action of any haloid in solution, very beautiful colourations are obtained. The experiment succeeds best with substances that easily give up the halogen, such as sodium hypochlorite, ferric chloride, iodine dissolved in potassium iodide, &c. But indications are also obtained with alkaline salts, such as ammonium chloride, &c., though more slowly and less brilliantly. With sodium hypochlorite the colours are often magnificent intense shades with metallic reflections, reminding one of the colours of a peacock's tail. Blue is the predominating tint. These are interference colours, caused by thin films, but whether of a normal silver haloid or a hemi-salt cannot be said. When silver leaf (normal silver) is fastened to paper and a comparative trial is made, the contrast is very striking. This matter will be more particularly examined in the second part of

* *Am. Chem. Journ.*, vi., 407 ; viii., 196.
† *Berichte der D. Ch. Ges.*, xx., 983.
‡ *Ibid.*, xx., 1458.
§ *Ibid.*, xx., 2288.

this paper, and is mentioned here as one of the reactions distinguishing allotropic from ordinary silver.

3. *The Action of Acids.*—The stronger acids, even when much diluted, instantly convert the allotropic forms of silver into normal grey silver; even acetic acid, not too much diluted, does this. It is important to remark that this change takes place absolutely without the separation of gas. I have more than once watched the whole operation with a lens, and have never seen the minutest bubble escape.

4. *Physical Condition.*—All these allotropic forms of silver are easily reduced to an impalpable powder. One is surprised to see what is apparently solid burnished metal break easily to pieces, and by moderate trituration yield a fine powder.

(To be continued).

NOTICES OF BOOKS.

Commercial Organic Analysis. A Treatise on the Properties, Proximate Analytical Examination, and Modes of Assaying the Various Organic Chemicals and Products Employed in the Arts, Manufactures, and Medicine, &c.; with Concise Methods for the Detection and Determination of their Impurities, Adulterations, and Products of Decomposition. By A. H. Allen, F.I.C., F.C.S. Second Edition, Revised and Enlarged. Vol. iii., Part I.—Acid Derivatives of Phenols, Aromatic Acids, Tannins, Dyes, and Colouring Matters. London: J. and A. Churchill.

Mr. Allen's great work is very far from declining in value and interest as it approaches completion, and is characterised both by general accuracy and by completeness.

In speaking of zinc phenol sulphonate the author notices a curious instance of blundering in high places. The British Pharmacopœia, after directing this salt to be prepared by "heating a mixture of carbolic acid and sulphuric acid, saturating with zinc oxide, evaporating, and crystallising," remarks that the solution of the product is "only rendered faintly turbid by chloride of barium."

We notice a curiously named mixture, "dextro-saccharine," which is simply commercial glucose got up with a small proportion of Fahlberg's saccharine. The product is said to be indistinguishable in taste from the best cane sugar. If this is correct as regards human taste, bees would very soon detect the imposture.

Among the varieties of tannin, tabulated on p. 79, we notice an animal tannin present in the corn-weevil. A similar compound, according to the *Transactions and Proceedings of the Entomological Society* for 1887 (xxxiii.), has been found in a variety of beetles which feed on vegetable matter. The author very clearly points out the improbability—not to say the impossibility—of devising any method for the accurate determination of tannins in all kinds of tanniferous matters.

In the section on writing-inks we find no mention of the useful method of comparing specimens of writing by different lights (sun-light, gas, monochromatic flames, &c.) if it is desired to ascertain the identity or diversity of the inks used.

The bulk of the book is taken up with a very elaborate account of dyes and colouring matters. After general remarks on the constitution of colouring matters, their relation to textile fibres, to mordants, and on their colouration, these compounds are described under the following heads:—The nitro- and nitroso-groups, the aurine class, the phthaleines, the azo-dyes, the rosanilines, the safranine group, the anthracene colours, and the sulphuretted and unclassified coal tar dyes. In this last class figures a compound bearing the name curcumene, which is objectionable on the same principle as are tropæoline and, in former days, roseine, azaleine, &c., names now obsolete or obsolescent because deceptive.

The colouring-matters of natural origin are very fairly described. The author justly remarks that the methods for extracting and producing such colours would have been greatly improved of late years had not the attention of tinctorial chemists been monopolised by the coal-tar colours. We are, indeed, convinced that, at least as far as indigo is concerned, there is good prospect for improvements of this kind. The ammonia process and the selection of ferment-cultures both are exceedingly promising. A foot-note states that, by the addition of ammonia to the leaves during fermentation, the yield of colour may be increased 100 per cent.

Concerning woad it must be remarked that it is used not so much for the trace of indigotine which it contains as for the favourable influence which it exerts on the fermentation in the warm vat.

Attention is called to the important fact that when indigo is reduced to indigo-white in the vat, and re-oxidised to indigo-blue on exposure to the air, a certain proportion is never recovered. The author suggests this loss as an interesting and possibly remunerative subject for investigation.

We regret that Mr. Allen retains the name indigo-carmine for extract of indigo. We submit that the name "carmine" should be strictly confined to the well-known preparation of cochineal, and not extended to coloured pastes in general.

We notice with satisfaction that the so-called "close" red woods, santal-wood, barwood, camwood, and calliatura, are clearly distinguished from the soft or open red woods, such as brazil-wood, peach-wood, sapan, &c. In some works, written by supposed practical men, we have known these classes to be confounded.

The author next gives in three successive chapters instructions for the recognition of colouring matters for the examination of commercial dyes and for that of dyed fibres. These chapters will be found exceedingly valuable.

CORRESPONDENCE.

THIOCAMF.

To the Editor of the Chemical News.

Sir,—No one who has any acquaintance with the liquid which Dr. Emerson Reynolds has named "Thiocamf" will question its value as a disinfectant. This liquid is not a novelty. In 1846, Parkes patented the preparation "obtained by passing sulphurous acid gas over finely granulated camphor until the camphor becomes liquid (by the absorption of sulphurous acid gas)." It was proposed to use this as a solvent of india-rubber, gutta percha, resins, &c. (see Specification, No. 11,147, A.D. 1846).

Indiarubber, when acted on by this liquid, is altered in precisely the same way as when acted on by dry sulphurous acid gas. There is no difficulty in preserving the liquid in a closed bottle, but if a piece of sheet indiarubber be wetted with it, the sulphurous acid is absorbed, leaving an efflorescence of camphor. Its effect on certain vegetable oils is curious and interesting.—I am, &c.,

Thomas T. P. Bruce Warren.

Tamworth Villa, Earlham Grove,
Forest Gate, E.

Examination of Manna.—A. Kresnel (*Pharm. Post* and *Chem. Zeitung*) dissolves one part of manna in one part of water, adds ten times the volume of alcohol at 95 per cent, heats to a boil, and filters through wool previously freed from fat. After the evaporation of the alcohol there remains pure mannite, which should form 75 per cent of a good manna.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 1, July 1, 1889.

On Barium Malonates.—M. Massol.—The author describes three neutral salts, the tetrahydrate, dihydrate, and the anhydrous compound. The dihydrate is of great stability, and if heated for some hours to 140° it retains the same composition.

The Acetates and Benzoates of the Active and the Racemic Camphols. Preparation of a Pure Dextro-Borneol Identical with the Borneol of Dryobalanops.—A. Haller.—This memoir does not admit of useful abstraction.

Zeitschrift fur Analytische Chemie. Vol. xxviii., Part 2.

Analytical Studies on Phosphododekamolybdic Acid: the Conditions of its Formation, and its Separation as an Ammonium Salt.—Dr. F. Hundeshagen.—The substance of this very extensive memoir will be given at some length.

Determination of Tungsten in Richly Tungstiferous Alloys.—Dr. Jos. Preusser.—From 0·5 to 1 grm. of the alloy, broken up in a steel mortar, finely pulverised, and sifted through lawn, is heated in a shallow porcelain capsule on a Bunsen burner, before the blast, or in the muffle, until the colour, which is at first greenish yellow, passes into a completely pure yellow. Over the Bunsen burner, this is generally effected in a few hours. No loss of tungstic acid is occasioned by excessive or prolonged ignition. The mass is then rinsed into a porcelain capsule and evaporated down once with aqua regia. It is then repeatedly evaporated to dryness with hydrochloric acid, and heated on the air bath to 120°. It is then taken up in dilute acid, let stand for some hours, and filtered. The tungstic and silicic acids left on the filter are ignited in a platinum crucible, after incineration of the paper, intimately mixed with 3—4 parts of sodium carbonate, and ignited before the blast for thirty minutes. When cold the melt is dissolved in hot water, filtered, and any tungstic acid not opened up is again fused with sodium carbonate. The filtrate, containing the tungstic acid as a sodium salt, is mixed with hydrochloric acid, when the tungstic acid separates out almost entirely as a white hydrate, but for its complete separation, the filtrate, after the addition of acid, must be evaporated down to dryness. It is then dissolved in water, and, after standing for a few hours, it is filtered by means of the filter-pump, and washed with a dilute solution of ammonium nitrate. The precipitate along with the paper is placed in an Erlenmeyer flask. Any hydrate adhering to the porcelain capsule is dissolved off by means of ammonia, and added to the contents of the flask, which are brought into solution as ammonium tungstate by the addition of ammonia and gentle heating on a hot plate. The silicic acid remains practically undissolved. The slight error due to the sparing solubility of silica in ammonia may be disregarded. The solution is freed by filtration from the silica evaporated down in a tared porcelain capsule, and the residue ignited until its weight is constant. If tin is present in the alloy the method of Donath and Müller is applicable. The metal is roasted, evaporated to dryness with aqua regia, heated to 120°, taken up in dilute acid, and the residue is treated according to the instructions of the authors above-mentioned, with the addition of the method just described for separating tungstic acid from silica.

The Analysis of Butter.—L. F. Nilson.—The substance of the author's process will be inserted as soon as practicable.

A Modification of the Kjeldahl Process.—Prof. J. W. Gunning.—Already inserted.

Examination of Commercial Peptones.—J. König and W. Kisch.—This memoir does not admit of useful abstraction.

On Polaristrobometric Chemical Analysis.—H. Landolt.—A treatise which first appeared in the *Transactions of the Royal Prussian Academy of Sciences* (1887, vol. xlviii.), and which is here given verbally. It does not admit of abridgment.

The Use of Potassium Manganate in Analysis.—Ad. Jolles.—(*Repertorium der Anal. Chemie*).

Separation and Determination of Zinc. J. Riban.—From *Bulletin Soc. Chimique de Paris.*

Separation and Determination of Boric Acid.—H. N. Morse and W. M. Burton.—From the *American Chemical Journal.*

Determination of Boric Acid.—S. L. Penfield and E. S. Perry.—From the *American Journal of Science.*

The Coloured Reactions of the Compounds of Carbon.—E. Nickel.—(An Inaugural Dissertation). Some of the reactions here mentioned will be inserted hereafter.

The Compositron of Wine Vinegars Obtained by Fermentation.—H. Eckenroth (*Pharm. Zeitung*).—The specific gravity of wine vinegars ranges between 1·0116 and 1·0149. If it falls below 1·0100 the presence of alcohol may be suspected, which is of rare occurrence. The extractive matter is between 0·35 and 0·51 per cent. Glycerin generally exists only in traces from 0·05 to 0·1 per cent. No constant relation between the proportions of glycerine and of acetic acid can be traced. The acetic acid is from 4 to 7 per cent, and in good samples does not fall below 6 per cent. Tartar is a main characteristic of a pure wine-vinegar, but for its determination 1 litre should be evaporated. The total ash rarely exceeds 0·25 per cent, and in most cases is not above 0·15.

Detection of Cochineal in Articles of Food.—Lagorge.—From the *Journal de Pharmacie et de Chimie.*

Examination of Balsam of Peru.—C. Donner (*Pharm. Central Halle*).—The author gives methods for detecting sophistications with benzoine and storax.

The Identification of Lanoline.—G. Vulpius (*Archiv. d. Pharmacie*) proposes the following reaction:—If a few centigrms. of lanoline are dissolved in chloroform, and if this solution is cautiously stratified above an equal volume of undiluted sulphuric acid in a test-tube, there appears at the contact of both liquids a fiery brown red ring. The chloroform above the ring has a violet reflection.

Determination of the Value of Ipecacuanha.—A. Lyons.—From the *American Journal of Pharmacy.*

Comparative Determination of Belladonna Leaves.—Coblentz.—From the *Pharmaceutical Journal.*

Valuation of Preparations of Strychnia, and Separation of Strychnine from Brucine.—O. Schweissinger (*Archiv der Pharmacie*).—No particulars are given.

Titration of Bitter Almond Water.—W. Kübel (*Arch. der Pharmacie*).—The author uses, instead of magnesium hydroxide, basic magnesium acetate.

Detection of Carbonic Acid in Potassa Lye.—A. Koster (*Archiv der Pharmacie*).—In a mixture of 10 c.c. saturated solution of gypsum and 5 c.c. distilled water potassa lye free from carbonate occasions no turbidity, whilst if one-fifth per cent of carbonate is present turbidity appears.

The Application of Nitroso-β-naphthol in Quantitative Analysis.—G. von Knorre.—Following out the methods which the author, in conjunction with Ilinski, has elaborated for separating cobalt and nickel, and also iron and aluminium, he has examined the behaviour of this reagent with other metals. It was found that in an acetic solution, besides cobalt and iron, copper is thrown down quantitatively by means of nitroso-β-naphthal, whilst aluminium, lead, cadmium, calcium, magnesium, manganese, nickel, mercury, and zinc remain in solution. The details of the various separations will be given hereafter.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Galvanising Iron.—Will some correspondent kindly recommend any books dealing with the process of galvanising iron, or refer me to titles and volumes of papers published on the subject?—ZINC.

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THE CHEMICAL NEWS.

Vol. LX. No. 1548.

ON RECENT RESEARCHES ON THE RARE EARTHS AS INTERPRETED BY THE SPECTROSCOPE.*

By WILLIAM CROOKES, F.R.S., &c.

(Continued from p. 30).

In the year 1886 (*Proc. Roy. Soc.*, xl., 502, June 9, 1886; Chem. News, liv., 27, July 19, 1886) I demonstrated from experiments on the fractionation of didymium that this element was very probably a compound capable of being resolved into a number of constituents, each represented by a single band, like the cases of yttrium and samarium, which give bands by phosphorescence. In Krüss and Nilson's case, the batch of crude earth contained in any single mineral was examined as a whole without any attempt to separate the earths, and the composition of some of these minerals is extraordinarily complex, euxenite for example containing, after removal of the other metals, the rare bodies Ce, La, Di, Sm, Yt, Er, Tr, Ho, Tm, Th, De, Sc, Dy, Be, Nb. Ta.

In my own case the didymium earths, upon which I formed the "one band one element" theory (Chem. News, liv., 27) were in a much more simple state, as the whole of the yttrium group, including erbium, holmium, thulium, &c., and others, had been removed, and the earth under examination probably contained little besides didymium and lanthanum, with traces only of samarium, yttrium, and calcium. But not even here was the earth under examination in a state of even approximate purity.

There are at least two points in these researches that I must touch, since they illustrate the necessity of great caution in drawing conclusions from an examination of absorption-spectra. Paul Kiesewetter and Krüss (*Ber.*, xxi., 2310; Chem. News, lviii., 75, 91) have recently published a paper on this subject, although it goes no further, nor indeed so far as the previous communication of Krüss and Nilson. They have examined gadolinite, and find that some constituents of didymium and samarium are absent, notably those which produce the group of lines in the green to which I have already referred. In my own laboratory I have worked for the last two years almost exclusively upon the earths from gadolinite—of which I have obtained a large quantity from Fahlun—and there is not the shadow of a doubt that in my gadolinite earths the lines reported absent by Kiesewetter and Krüss are present in abundance.

Some hitherto unexplained condition doubtless rendered these lines invisible to Kiesewetter and Krüss; perhaps the presence of some other earths, or some condition of concentration or acidity. In the light of this knowledge I do not see how we can take the results of Krüss and Nilson or my own as final.

Concerning the influence of one body upon another little is yet known, but that little is of sufficient importance to make us very careful how we interpret absorption-spectra when uncorroborated by chemical results. Lecoq de Boisbaudran and Smith have pointed out some important modifications produced in absorption-spectra by an excess of acid (*Compt. Rend.*, lxxxviii., 1167), and later on Soret (*Compt. Rend.*, September 15, 1879) verified these observations. Brauner and others have recorded experiments on mixing solutions of didymium and samarium; they find, in the case of a didymium solution showing the group of three bands, λ 476, 469, 428 ($1/\lambda^2$ 430·4, 441·3, 454·6), that by adding a dilute solution of samarium, all three of these bands vanish without any appearance of any of the samarium bands, until a certain proportion is reached, when the samarium bands gradually come in their place (Brauner, *Trans. Chem. Soc.*, 1883, xliii., 286). In my own experiments, I find that from a solution of erbia which originally shows no trace of the strong didymium band lying between λ 596 and 572 ($1/\lambda^2$ 281 and 305), appreciable quantities of didymium can certainly be squeezed out by fractionation.

Owing to its complicated nature, Kiesewetter and Krüss consider gadolinite an unfavourable source of didymium for these investigations, and recommend that a large quantity of earth from keilhauite should be systematically worked up, for the reason that keilhauite didymium is more simple in constitution.

The Erbium Group.

It is known that a certain oxide, ten years ago called erbia, and regarded as belonging to a simple elementary body, has been resolved by the investigations of Delafontaine, Marignac, Soret, Nilson, Clève, Brauner, and others into at least six distinct earths—three of them, scandia, ytterbia, and terbia, giving no absorption-spectra, whilst others, erbia (new), holmia, and thulia, give absorption-spectra.

In Fig. 8A I have represented the old erbium absorption-spectrum, as it was known down to the year 1878. In Fig. 8B, as in the case of didymium, I have given for diagrammatic purposes certain lines which, not seen in unfractionated erbia, belong to bodies capable of being separated from it by fractionation.

The first to announce that erbium was not a simple body was Delafontaine, who in 1878 (*Compt. Rend.*, lxxxvii., 559; Chem. News, xxxviii., 202) published an account of philippium, a yellow oxide characterised by a strong band in the violet, λ 400 to 405 ($1/\lambda^2$ 625, to 623), a broad, black absorption-band in the indigo-blue, λ about 450 ($1/\lambda^2$ 494), two rather fine bands in the green, and one in the red.

The history of philippium is curious, and I may perhaps be allowed to give it in some detail. A year after Delafontaine's discovery Soret (*Compt. Rend.*, lxxxix., 521; Chem. News, xl., 147) published a paper in which he declared that philippia was identical with his earth X. The next month, in a note on erbia, Clève (*Compt. Rend.*, lxxxix., 708; Chem. News, xl., 224) said he could not identify Soret's X with Delafontaine's philippia, as the latter was characterised by an absorption-band in the blue which occupied the same place as one of the erbia bands. In February, 1880 (*Compt. Rend.*, xc., 221; Chem. News, xli., 72), Delafontaine returned to the subject, enumerating 10 new earths in gadolinite and samarskite, viz., mosandra, philippia, ytterbia, decipia, scandia, holmia, thulia, samaria, and two others unnamed. He said that the properties of philippia were those of Soret's X and Clève's holmia, and proposed that the name "holmia," being a duplicate name for an already known earth, should be discarded in favour of philippia. In July, 1880 (*Compt. Rend.*, xci., 328; Chem. News, xlii., 185), Clève repeated his former statement that philippia was not the same body as Soret's X or holmia. Delafontaine next withdrew all he had said about the absorption-spectrum of philippium, and decided that it had no absorption-spectrum (*Archives de Genève*, [3], 999, 15). Finally, Roscoe (*Chem. Soc. Journ.*, xii., 277), in an elaborate chemical examination of the earth-metals in samarskite, proved that philippia was a mixture of yttria and terbia. From a prolonged chemical study of these earths I have since come to a similar conclusion; but a spectroscopic examination of the earth left on igniting some specially purified crystals of "philippium formate" tested in the radiant matter tube, has shown

* Address delivered by the President of the Chemical Society at the Annual General Meeting, March 21st, 1889.

me that in the separation of Delafontaine's philippium the yttria undergoes a partial fractionation, and three of its components or meta-elements, Gζ, Gδ, and Gβ, are present in great abundance, while others, Gα and Gη, are almost if not quite absent.

Shortly after the announcement of philippium, Soret (*Compt. Rend.*, lxxxvi., 1062) described an earth which he provisionally called X. This was soon found to be identical with an earth subsequently discovered by Clève (*Compt. Rend.*, lxxxix., 479; Chem. News, xl., 125), and called by him holmia. Soret admitted the identity, and agreed to adopt Clève's name of holmia. Fig. 9 shows the absorption-spectrum of X or holmia. It consists of a very strong band in the extreme red, λ 804 ($1/\lambda^2$ 155), two characteristic bands in the orange and green, λ 640 and 536 ($1/\lambda^2$ 244 and 347), besides fainter lines in the more refrangible part of the spectrum, and a number of bands in the ultra-violet.

Simultaneously with the discovery of holmia, Clève announced the existence of a second earth from erbia, which he called thulia. Fig. 10 shows the absorption-spectrum of thulia. It consists of a very strong band in the red, λ 680 to 707 ($1/\lambda^2$ 216 to 200), and one in the blue, λ 464·5 ($1/\lambda^2$ 462). The residual erbia, after separation of these earths, gives a simpler absorption-spectrum, shown in Fig. 11.

In 1886 (*Compt. Rend.*, cii., 1003, 1005) Lecoq de Boisbaudran showed by fractional precipitation of Soret's X and by spectroscopic examination of the simple fractions, that this X, or holmium, consisted of at least two elements, one of which he named dysprosium, retaining the name of holmium for the residue left after deducting dysprosium. Fig. 11 shows the absorption-spectrum of dysprosium; it has four bands, λ 451·5, 475, 756·5, 427·5 ($1/\lambda^2$ 490·5, 443, 175, 547). The new holmium gives an absorption-spectrum shown in Fig. 13.

As regards dysprosium, I pointed out (*Proc. Soy. Soc.*, xl., 502), at the time it was first announced, that I had obtained a solution in which one of the bands claimed for dysprosium, the one at λ 451·5 ($1/\lambda^2$ 490·5), was very strong, while the others were absent. As M. de Boisbaudran associates the bands at λ 475 ($1/\lambda^2$ 443) and λ 451·5 ($1/\lambda^2$ 490·5) as both belonging to dysprosium, and as I have obtained an earth which gives λ 451·5 ($1/\lambda^2$ 490·5) strong with no trace of λ 475 ($1/\lambda^2$443), it is evident that the conclusion I arrived at in 1886—that dysprosium itself consisted of at least two simpler bodies—is correct.

The old spectrum of erbium (Fig. 8) shows two faint bands at λ 550 and λ 493 ($1/\lambda^2$ 331 and 409); the second being broader than the first. These bands do not occur in the spectra of holmium, thulium, dysprosium, or the new erbium. In a long-continued fractionation of the erbia group of earths, carried out with an ample supply of the old erbia, I find an earth giving these two bands concentrating at one end, and the bands become stronger. At the same time two other new bands are making their appearance. This, therefore, points to the existence of still another earth belonging to the erbium group.

Incandescence Spectra.

Another distinct method of spectrum analysis depends on the examination of the spectrum of the light emitted by a solid substance when raised to incandescence. Almost the only known example of this is obtained in the case of erbia (*ibid*, xl., 77, January 21, 1886). It is scarcely known that if erbia in the solid state is illuminated by the electric or other bright light, and examined in the spectroscope, it gives a spectrum of black lines and bands as distinct as the Frauenhofer lines. The spectrum of bright lines emitted when solid erbia is heated to incandescence in the blowpipe flame has been more often observed; in this case the lines come out luminous on a faintly continuous background, whilst the reflection spectrum just mentioned is composed of black lines sharply defined and much more luminous, upon a continuous spectrum. Holmia and thulia, components of old erbia, possess a similar property (Chem. News, lvi., 165).

Phosphorescence Spectra.

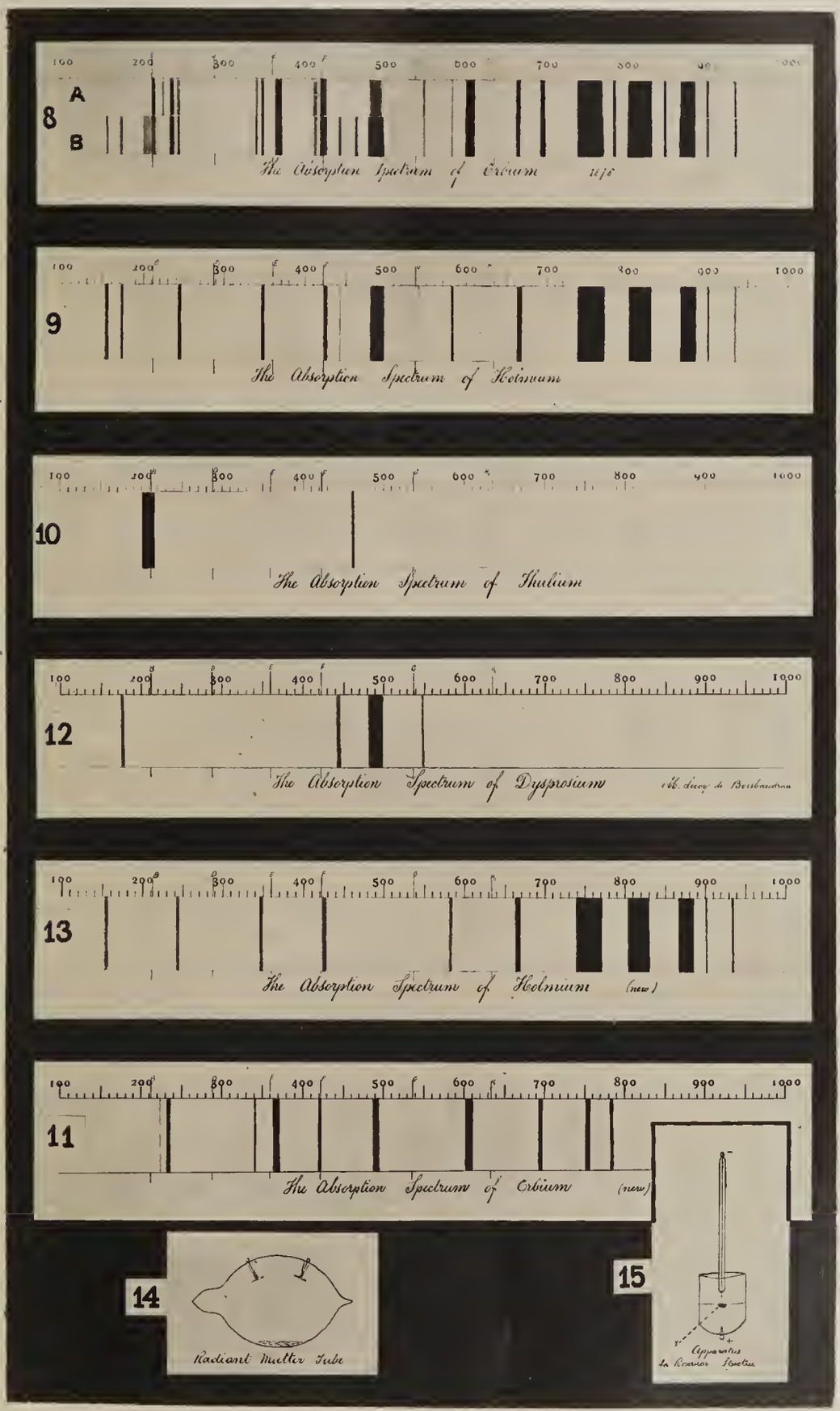
I will now deal with phosphorescence spectra. Not a few chemists and physicists, conspicuous among whom is Ed. Becquerel, have carefully studied the phenomena of phosphorescence. Phosphorescence may be excited by elevation of temperature, by mechanical action, by electricity, and by exposure to the rays of the sun, and the light thus given off—for example, in the case of fluor-spar, has been examined by means of the spectroscope. In my own spectroscopic research I have dealt with the phosphorescence occasioned by the impact of the molecules of radiant matter upon certain phosphorescent bodies, or what I have ventured to call molecular bombardment.

It is not necessary for me to describe the mode of procedure further than to say that the substance under examination is placed in a very high vacuum—a vacuum which varies in degree in the case of certain earths. Fig. 14 shows the form of radiant matter tube I prefer. In such a vacuum, when submitted to the action of the induction current, substances phosphoresce very differently from what they do when treated similarly at the ordinary pressure of the atmosphere. Under such circumstances the spectroscopic examination of matter affords what I have called the radiant matter test. The number of substances which are thus phosphorescent is very considerable. Glass of different kinds, according to its composition, phosphoresces with various colours. Phenakite (glucinium silicate) phosphoresces blue; spodumene (aluminium and lithium silicate) gives off a rich golden-yellow light, whilst the emerald phosphoresces crimson, and the diamond, being exceptionally sensitive and brilliant, throws off a bright, greenish white light.

The ruby, one of the minerals I examined earliest in this manner, glows with a rich, brilliant, red tone, quite independent, as regards its depth and intensity, of the colour of the stone as seen by daylight; the pale, almost colourless specimens, and the highly prized variety of the true "pigeon's blood," all phosphoresce with substantially the same colour.

There are several varieties of phosphorescence spectra, or rather, substances to be submitted to the radiant matter may be previously prepared in divers manner, so as to give modified results. Thus—

a. An earth alone—of course in the solid state—may be very strongly ignited, and, when cold, examined in the radiant matter tube. This method differs from the use of the spectrum of incandescent solids above noticed, solely in the final test of molecular bombardment. Of this variety of phosphorescence spectra, we may take, as examples, the phenomena yielded by alumina, yttria, didymia, and lanthana.

b. Another modification applicable in the treatment of the less pure earths takes as material the sulphates of the earths. The substance under examination is first treated with strong sulphuric acid; the excess of the acid is then removed by heat, and, lastly, the sulphate is heated to a point just short of driving off all the sulphuric acid. It is then placed in the radiant matter tube, and when the exhaustion has been carried as far as necessary, the induction current is passed through (*Phil. Trans.*, Part III., May, 1883). This method gives a spectrum of broad bands, easily recognised, but by no means easy to measure. The spectroscope used should have a low dispersive power, and should not have a very narrow slit. In the case of yttrium sulphate the bands are more analogous to the absorption-bands seen in solutions of didymium than to the lines given by spark spectra. If examined with a high magnifying power the outlines of the bands become less definite. The bands are seen much more sharply when the current first passes than after it has been passing for some time and the earth has become hot. On cooling, the bands again appear sharply defined.

SPECTROSCOPIC RESEARCHES ON THE RARE EARTHS.
W. CROOKES.

This method of observing the constitution of the rare earths, duly aided by delicate and prolonged chemical processes, has permitted us to push our investigations further than had previously seemed practicable. It enables us to determine whether we have reached the end of our investigations—a consummation which had hitherto been vainly sought. It has enabled us to prove that yttrium, samarium, &c., are not simple, homogeneous bodies. But what of the constituents into which they have been thus resolved? Suppose we refine them down until each displays merely one spectral band—what then? Is each one of such bodies barely differentiated from its neighbours chemically or physically, entitled to rank as an element? If so, as I pointed out in the Address which I had the honour to deliver before you in March last, we shall have to deal with further perplexing questions, arising in part from the relation of such elements to the periodic system. In a discussion of the elements, not as yet published, Dr. Wundt maintains that their possible number cannot exceed 79. But I myself see no definite and sufficient reason for limitation to this number. If these bodies are not elementary, possessing as they do the properties commonly regarded as characteristic of an element, we must be prepared to show why not?

Whatever rank may ultimately be assigned to these substances, they must, for convenience sake, have names as soon as our knowledge of their properties is in a sufficiently advanced state to allow of their removal from the suspense account.

(To be continued).

THE ANALYSIS OF GLASSES.

By DAVID LINDO.

(Concluded from p. 33).

The Lime and Magnesia.

The solution containing ammonium sulphide (in order to precipitate the manganese) was made up to 200 c.c. and filtered. 100 c.c., equal to 1 grm. of glass, was taken to estimate the lime and magnesia. HCl was added in slight excess and the liquid was concentrated and filtered; ammonia in excess was then added and ammonium oxalate. The mixture was set aside for several hours, filtered, generally through a small Gooch, and the filtrate was tested for magnesia by adding powdered microcosmic salt in large excess and stirring well. If more than traces of magnesia are present the calcium oxalate is dissolved in HCl, re-precipitated, filtered, and the filtrate is added to the liquid in which the bulk of the magnesia was precipitated. The calcium oxalate is ignited, gently at first, and is then reduced to lime by the blast. The magnesia is obtained as pyrophosphate by strong ignition over the spirit-lamp.

Of the 200 c.c. solution 50 c.c. were filtered, acidulated with HCl, concentrated, filtered, mixed with 10 c.c. ferric chloride solution of known strength, precipitated with ammonia in heat to recover last trace of silica. If the lime was first removed by oxalate the excess of the latter in the filtrate renders the ferric oxide very difficult to wash, and a trace of silica may possibly be carried down with the lime. When the lime was removed in one experiment the iron precipitate weighed only 0·001 less than when the lime was left in. In glass containing moderate quantities of lime the author has therefore not removed this before recovering the silica. The last fraction of the 200 c.c. solution, including the washings of the filter, was kept in case of accident.

No. 28.—Lime, 4·92 per cent; magnesia, 0·27 per cent.

No. 34 A.—Lime, 6·04 per cent. Magnesia, trace only, not determined.

No. 34 B.—Lime, 6·06 per cent. Magnesia, trace only.

No. 3.—Lime, 8·76 per cent. Magnesia, trace only.

No. 1.—Lime, 4·02 per cent; on repeating operation, 3·96 per cent. Magnesia, imponderable.

No. 5.—Lime, 5·62; magnesia, 0·21.

No. 31.—Lime, 8·16. Magnesia, trace.

No. 29.—Lime, 5·96. Magnesia, trace.

No. 22.—Lime, 6·32. Magnesia, trace.

No. 10.—Lime, 9·96. Magnesia, trace.

No. 8.—Lime, 7·22. Magnesia, trace.

The following table shows the complete analysis of some of the specimens:—

No. 3.	
K_2O	2·27
Na_2O	15·75
Lime	8·76
Ferric oxide	0·22
Alumina	1·11
Silica	70·61
	98·72
No. 10.	
K_2O	2·08
Na_2O	15·68
Lime	9·96
Ferric oxide	0·30
Alumina	2·01
Silica	68·94
	98·97
No. 28.	
K_2O	10·08
Na_2O	10·70
Lime	4·94
Ferric oxide	0·29
Phosphoric acid	0·14
Silica	73·13
Magnesia	0·27
	99·55
No. 22.	
K_2O	0·30
Na_2O	19·40
Lime	6·32
Ferric oxide	0·30
Silica	73·06
	99·38
No. 34 A.	
K_2O	4·02
Na_2O	16·84
Lime	6·04
Ferric oxide	0·42
Alumina	2·29
Silica	69·86
	99·47
No. 29.	
K_2O	5·44
Na_2O	13·62
Lime	5·96
Ferric oxide	0·36
Alumina	2·00
Silica	71·49
	98·87
No. 8.	
K_2O	1·80
Na_2O	19·18
Lime	7·22
Fe_2O_3	0·27
Al_2O_3	2·37
Silica	67·23
	98·07

No. 31.

K_2O	0·66
Na_2O	15·22
Lime	8·16
Fe_2O_3	0·19
Al_2O_3	0·83
Silica	73·70
	98·75

No. 1.

K_2O	4·68
Na_2O	14·38
Lime	4·02
Ferric oxide..	0·21
Alumina	2·48
Silica	72·49
	98·26

CHEMISTRY UNDER HIGH PRESSURE.

By H. N. WARREN, Research Analyst.

Of all the forces that the chemist is able to bring to bear upon or aid in his investigations, perhaps none is more important or stands less rivalled than that of force in its simplest form, namely pressure; and with respect to this agent no form is apparently more indicated to aid in scientific research than that evolved automatically, or more correctly speaking by encouraging a portion of the substance under examination, contained in a suitable enclosure, to considerably expand, through subjecting the same to a more or less elevated temperature, and by so doing either retard or prevent further dissociation of the remaining portion in consequence of the pressure thus exerted. This particular form of operation, as is well known, is frequently adopted for the decomposition of farinaceous substances, when desirous of converting the starch present into that of glucose, previous to estimating the same.

The mode of construction of these tubes and the manipulation of the same have already been described (Chemical News, vol. lviii., 155). Since that period, however, a somewhat more robust apparatus has been made use of, and intended for dry heats. The plan of construction being almost essentially the same as in the former instance, save that the copper casement is replaced by that of wrought iron, to the extent of four inches thick, being provided with a drilled orifice of half an inch circumference, and extending to within an inch of the bottom, inside of which is inserted a small platinum or porcelain tube, according as the nature of the experiment may command. The platinum tube with its contents being hermetically sealed before the oxyhydrogen blowpipe, and after inserting the same packed with dry magnesia, the top being afterwards closed by the aid of a powerful screw extending within the orifice to the length of two inches, and terminating in a handle, so as to ensure of sufficient leverage power being applied to readily expose the contents after cooling.

In order to test the efficiency of the apparatus the inner or platinum tube was half filled with pure precipitated calcium carbonate, closed, and heated to whiteness by the aid of a wind-furnace. On opening the same, after cooling, a stick of perfectly fused substance was obtained, possessing all the properties of marble, being somewhat more translucent. By substituting for the platinum a porcelain tube, at the same time using a somewhat lower temperature, arsenicum metal was readily fused, and presented considerable lustre. Among various other experiments may be mentioned the decomposition of potassium silicon fluoride when in admixture with zinc, from which the silicon was afterwards separated in the form of fine needle crystals. A modified form of apparatus is at present under construction in which both the temperature and pressure may be lowered at will. Several interesting results have been already obtained, and it is hoped to ultimately lead to some improvements in organic synthesis.

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ON THE

STABILITY OF THE FATTY GLYCERIDES.

By THOMAS T. P. BRUCE WARREN.

I omit from the present consideration animal oils and fats generally, and include all the vegetable fixed oils which I have had an opportunity of working on, which are fluid at 15·5° C.

It is customary to divide oils into two classes, viz., drying and non-drying oils. Anyone who has given attention to this subject must feel that this division is wanting in scientific precision. So long as it is a question relating to oils suitable for making paints this division may be technically useful, but if we go further into the matter of lubricants we must confess that there is an absence of that demarcation between the two classes of oils, as implied strictly by this division.

The drying or clogging properties of an oil depend mainly on its stability. An oil will not dry or clog until it is decomposed, and in proportion to the rapidity of this change so is the drying quality of an oil increased. The general explanation is that the glycerin is oxidised into carbonic acid and the fatty acids into a thickened mass or dry product.

Cotton and rape-seed oils decidedly thicken when heated air or oxygen is passed into them, especially if the oils themselves are heated to 300° C. Oils of poppy-seed and walnuts will thicken readily on exposure to warm air; olive oil does not thicken under the same circumstances.

When an oil is oxidised, its iodine absorption is diminished, whilst its electrical resistance is increased. The product obtained with sulphur chloride is very dark, in some cases almost black.

Although I have passed ozonised oxygen into pure olive oil for days under exposure to strong sunlight, I have not been able to obtain a product with sulphur chloride darker in colour than that obtained from the original oil. I therefore conclude that pure olive oil has a very remarkable stability when compared with other oils.

Oils which have parted with a portion of their glycerin will yield a product containing a larger portion of matter soluble in carbon disulphide than the same oil when fresh. Cotton-seed oil, deprived of its glycerin is readily soluble after treatment with sulphur chloride.

The effects of heat on oils show that olive oil is more stable than sesame oil.

The non-suitability of an oil as a lubricant may be ascertained by the diminished iodine absorption when oxygen is passed into it. An oil which "gums" or clogs on a bearing will be found to have its iodine absorption diminished in proportion to its tendency to clog. The value of this as a test for a machine oil or lubricant is of very great importance, especially if a proper mechanical arrangement is not available for testing.

The thickening of an oil on a bearing depends on its stability. We have, on a rapidly revolving spindle, every facility at its bearings for oxidation. In an extreme case the oil becomes quite sticky when the journals have cooled down. As friction involves extra work to be done, it is obvious that an oil which reduces this to a minimum must be one which, besides reducing friction, does not involve internal work on itself. Many adulterations may be recognised by carefully observing the effects of friction on a journal provided with a thermometer.

ON ALLOTROPIC FORMS OF SILVER.*

By M. CAREY LEA, Philadelphia.

(Continued from p. 36).

A. *Soluble Allotropic Silver.*

A solution of ferrous citrate added to one of a silver salt produces instantly a deep red liquid. (Ferrous tartrate gives the same reaction, but is less advantageous). These red solutions may either exhibit tolerable permanency or may decolourise, letting fall a black precipitate. It is not necessary to prepare the ferrous salt in an isolated form, a mixture of ferrous sulphate and sodic citrate answers perfectly.

When, however, concentrated solutions are used with a large excess of ferrous sulphate, and a still larger one of alkaline citrate, the liquid turns almost completely black. It should be stirred very thoroughly for several minutes to make sure that the whole of the precipitated silver citrate is acted upon by the iron. After standing for ten or fifteen minutes the liquid may be decanted, and will leave a large quantity of a heavy precipitate of a fine lilac-blue colour. It is best to adhere closely to certain proportions. Of a 10 per cent solution of silver nitrate, 200 c.c. may be placed in a precipitating jar. In another vessel are mixed 200 c.c. of a 30 per cent solution of pure ferrous sulphate, and 280 c.c. of a 40 per cent solution of sodic citrate. (The same quantity of ferrous sulphate or of sodic citrate in a larger quantity of water will occasion much loss of the silver product). I think some advantage is gained by neutralising the ferrous solution, which has a strong acid reaction, with solution of sodium hydroxide: as much may be added as will not cause a permanent precipitate. To the quantities already given, about 50 c.c. of 10 per cent soda solution. The reaction takes place equally well without the soda, but I think the product is a little more stable with it. The mixed solution is to be added at once to the silver solution.

The beautiful lilac shade of the precipitate is rather ephemeral. It remains for some time if the precipitate is left under the mother-water, but when thrown upon a filter it is scarcely uncovered before the lilac shade disappears and the precipitate takes a deep blue colour without losing its solubility. It may be washed either on a filter or by decantation with any saline solution in which it is insoluble and which does not affect it too much. On the whole, ammonic nitrate does best, but sodic nitrate, citrate, or sulphate may be used, or the corresponding ammonia salts. Although in pure water the precipitate instantly dissolves with an intense blood-red colour, the presence of five or ten per cent of any of these salts renders it perfectly insoluble. I have usually proceeded by adding to the precipitate (after decanting the mother-water as completely as may be, and removing as much more as possible with a pipette) a moderate amount of water; for the above quantities about 150 c.c. Much less would dissolve the precipitate but for the salts present: this much will dissolve the greater part, but not the whole, which is not necessary. A little of a saturated solution of ammonic nitrate is to be added, just enough to effect complete precipitation.

As the material appears continually to change, the amount of washing needed must depend upon the object in view. If wanted for analysis, the washing must be repeated many times until ferric salt ceases to come away, but no amount of washing will entirely eliminate it. After seven or eight solutions in pure water and as many precipitations, the material is to be thrown on a filter, the liquid forced out as completely as possible with a pump, and then the ammonic nitrate washed out with 95 per cent alcohol until the filtrate leaves nothing on evaporation. The substance at this point is still soluble in water, though much less so than at first. During the washing the solubility slowly but steadily diminishes, a fact rendered noticeable by less and less ammonic nitrate being needed to precipitate it from its solution.

Analysis.—The product after thorough washing, as above described, with alcohol, was dried at ordinary temperatures or a little above, and was then reduced to very fine powder and washed again with water as long as anything dissolved. It was then dried at 100° C. in water-bath. Three silver determinations were made—

A1	.. .. ..	97·31 per cent silver
A2	.. .. ..	97·18 ,, ,,
B	.. .. ..	97·21 ,, ,,

A1 and A2 were made with different portions of the same material, B with different material prepared in exactly the same way.

The substance therefore contained on an average 97·27 per cent of silver. The nature of the residue would decide whether the material was silver with a certain amount of impurity firmly attached to it, or whether we had to do with silver in chemical combination with other elements.

The filtrate from the silver chloride in analysis A2 was evaporated to dryness, and was found to contain chiefly iron and citric acid. The iron was thrown down as sulphide, re-dissolved in nitric acid, precipitated hot, washed with boiling water, and gave 0·8947. The residue therefore consisted of ferric oxide and citric acid, probably in the form of ferric citrate, and attached so strongly that even the very careful and prolonged washing given failed to remove them. Stronger means would be required than could be used without altering the condition of the substance. The conclusion, therefore, seemed to be justified that the material consisted of uncombined silver simply mixed with impurity.

To verify this conclusion by additional evidence, the substance was examined as to its behaviour when heated. For if any other element were chemically combined with the silver it would only be (in view of the high percentage of silver) hydrogen or oxygen. We might have to do with a hydride, analogous to Wurtz's hydride of copper, or possibly an oxide, but not probably as Ag_4O would contain only 96·43 per cent of silver.

The presence of either hydrogen or oxygen in combination with silver seems to be pretty certainly negatived by the action of dilute sulphuric acid on this (and the two other substances, B and C, to be described farther on). They are all converted into grey metallic silver without the slightest escape of gas. This seems tolerably conclusive in itself, and the result of exposing a great number of specimens of all the forms A, B, and C to the action of heat, was equally so. As the object was to expose the fresh and moist material to a gradually increasing heat from that of boiling water to a low red heat without interrupting the process, the following arrangement was found convenient:—

A piece of Bohemian glass tube about six inches long was sealed in the lamp at one end, the other closed with a rubber cork, through which passed a small gas delivery tube, and another tube passing into a small test-tube partly filled with water and having another tube through the cork passing under the surface of the water, thus preventing regurgitation. The material was thus first exposed for some hours to a heat of about 150° C. in a chloride of calcium bath; this was next removed, and the heat continued to low redness. Only traces of gas were evolved, and this was found to be in all of the many trials made, carbonic acid, derived from the citric acid adhering. This treatment was repeated many times with all the different varieties of the substance, and with the same result. The temperature was always raised sufficiently high to ensure the complete conversion of the material into normal grey silver, but in no case was oxygen or hydrogen set free.

It could not be overlooked that in all these trials the material had passed into an insoluble form before the silver determination was made. There remained, there-

* *American Chemical Journal*, Vol. xxxvii., No. 222.

fore, this possibility: that the silver, so long as soluble, might be in combination with citric acid, and that its change to the insoluble condition was caused by its separating from the citric acid. It seemed desirable that this view should be tested. As the object was to determine the condition of the silver in the substance as originally formed, avoiding as far as possible to change that form by attempts at purification, the only course available was to determine the ratio between the silver on the one hand and the citric acid on the other, either excluding from the determination, or else removing, that portion of the citric acid which was combined with sodium (sodic citrate being used in excess) or with iron. The first attempt was to exclude without removing it, by using Wolcott Gibbs's ingenious method of precipitating the base by hydrogen sulphide, and determining the acid thus set free in a solution originally neutral. It was ascertained by careful experiment on weighed quantities of pure anhydrous citric acid, that exact titration could be made with the aid of phenolphthalein. The silver was next re-dissolved and estimated as chloride. A large number of determinations were made, but the method proved unsatisfactory. It was found that portions of the same material operated upon separately gave different (even widely different) results. In fact, this very discordance was in itself a proof than to stœchiometrical combination existed between the silver and the citric acid.

The importance of the matter led me to take it up again with different means, estimating the citric acid by Creuse's method. In this method the solution, after being reduced to a small bulk, is exactly neutralised (with ammonia or acetic acid), is treated with a slight excess of barium acetate, and then mixed with twice its bulk of 95 per cent alcohol, let stand a day, and filtered and washed with 65 per cent alcohol. In igniting, a few drops of sulphuric acid convert the barium salt into sulphate, in which form the estimation is made. A preliminary trial with a weighed quantity of citric acid showed that this method gave fairly good results. I was obliged to vary the method somewhat: the precipitate of barium citrate carried down with it enough iron to render it ochrey in appearance. It was, therefore, after thorough washing with 65 per cent alcohol till every trace of barium acetate was removed, dissolved on the filter with dilute hydrochloric acid (acid 1, water 10), in which barium citrate is extremely soluble and washed through. This was followed by still weaker acid, and finally with water. From the filtrate, sulphuric acid precipitated snow-white barium sulphate.

But this method requires that both the sulphates and the excess of sodic and ferric citrate shall first have been perfectly removed. The blue precipitate was therefore washed with dilute solution of ammonic nitrate until this was effected. The necessity for this purification was regrettable as introducing a possibility of a change during the treatment. It was, however, indispensable that the ferrous, ferric, and sodic citrates present should be got rid of. The material after this treatment was still freely soluble in water, to a dark red solution. An examination of its absorption spectrum showed it to be still a true solution. From this solution the silver was first removed by H_2S, and then the citric acid was determined in the above described way. (If the silver were thrown down by hydrochloric acid, the reliability of the citric determination would be impaired). Next, the silver sulphide was converted into chloride and weighed. The result gave the ratio—

1 grm. silver to 0·03195 grm. citric acid.

In this case washing out the sulphates, &c., was an affair of several days. The work was repeated, reducing the time as much as possible. The material was precipitated, decanted as soon as settled, thrown upon a filter-pump, and the funnel kept constantly full of ammonic nitrate in dilute solution by a wash-bottle. By using very thick paper and a powerful pressure the entire washing was rapidly finished, so that in about six hours from first precipitation the material was thoroughly washed, re-dissolved, and again filtered and placed under the action of H_2S. The result was—

1 grm. silver to 0·0130 citric acid.

When these relations are reduced from weights to equivalents they become—

No. 1. 1 equiv. citric acid to 55·63 equivs. silver,
No. 2. 1 ,, ,, ,, 193·7 ,, ,,

indicating both that the proportion of citric acid present is variable, and that it is certainly not in stoichiometrical combination with the silver in the substance examined.

It has been already said that these solutions, before being acted upon by H_2S, were examined optically and found to be true solutions. The inference, therefore seems to be very strong that there exists an allotropic form of silver freely soluble in water. This is a property so exceptional in a metal that I have admitted it with much hesitation. The principal arguments are as follows:—

The content of silver in the various products was very carefully and, I believe I may say, quite accurately determined; it was extremely high, always above 97 per cent. As already remarked, this virtually excludes the presence of all elements except hydrogen, and possibly oxygen. These elements were carefully searched for, but their presence could not be detected. To suppose that we had to do with a mixture in which some compound of silver was mixed with metallic silver was not possible, for as the whole was soluble we should still have to admit the solubility of silver.

We have consequently to deal with a substance containing over 97 per cent of silver, and neither hydrogen nor oxygen in combination with it, the remaining 2 or 3 per cent fully accounted for by ferric oxide, and citric acid determined as present as accidental impurity; the substance itself readily amalgamating with mercury by simple friction, nevertheless abundantly soluble in water. If I had been able to find any other explanation for these facts without admitting the solubility of silver, I should have adopted it. But none presented itself.

Whether in solution it exists as a hydrate, that is, in more intimate combination with one or more equivalents of water, cannot be said with entire certainty; but the easy amalgamation with mercury seems hardly to favour that view. No means could be found for settling the question absolutely. Certainly at 100° C. all water is expelled, but this is, of course, not an argument. All the water is not expelled by indefinite exposure to a vacuum over sulphuric acid. But the proportion left is very small.

The material examined was in all cases as nearly as possible the same as that originally precipitated, but absolute identity could not be obtained. The purification absolutely necessary effects some change. This is shown by the colour. The freshly precipitated material dissolves to a blood-red liquid, by great dilution yellowish red. The purified substance gives a darker red solution, which with dilution remains still red. Of the nature of the substances in the condition in which they were analysed, I can speak with some positiveness, and these include a substance soluble in water and, nevertheless, appearing to be nearly pure silver.

The constitution of the lilac-blue substance at the moment of formation, and whilst still under its mother-water, is a matter of more difficulty; it could not be said with certainty that it was not in some way altered in the purification. Much time and labour were spent in endeavouring to settle this point, without entirely satisfactory results, and I am at present engaged in the search for a better method.

When this blue soluble substance, purified either by washing very moderately by ammonium nitrate or by washing with pure water, using those portions which remain undissolved after most has been carried through the

filter, is brushed over paper and dries rapidly, it exhibits a very beautiful succession of colours. At the moment of applying, it appears blood-red; when half dry, it has a splendid blue colour with a lustrous reflection; when quite dry, this metallic effect disappears, and the colour is mat-blue. Examined with a polariser, it shows the same characters as to two reflected beams of light polarised in planes perpendicular to each other that are described further on under B.

When the blue substance prepared in either way dries more slowly in lumps, the result is very variable; sometimes it is bright bluish metallic; sometimes dull red colour, with a metallic reflection only where it has dried against a smooth surface.

(To be continued).

DERIVATIVES OBTAINED FROM MONOCHLORDINITROPHENOL AND BASES OF THE AROMATIC SERIES.*

By EDGAR F. SMITH.

It is well known that picric acid combines readily with bases and the higher hydrocarbons of the aromatic series to form well-crystallised and stable compounds. It has, however, not been observed that phenols containing less than three nitro-groups together with other negative groups or elements, possessed this acidic property of picric acid. Several years ago (*Am. Chem. Journal*, i., 180) I discovered that when monochlordinitrophenol (1 : 2 : 4 : 6) and aniline were brought together there resulted a rather stable derivative, which did not decompose in aqueous solution until after prolonged boiling. Recently I have obtained derivatives with this same chlordinitrophenol and the bases and hydrocarbon mentioned below.

The phenol itself forms yellow-coloured needles, melting at 80° C. Its *α-naphthylamine* derivative consists of brownish yellow crystalline tufts, composed of velvety needles, melting at 131° C. and solidifying at 110° C. It was obtained by dissolving equal quantities of the phenol and α-naphthylamine in hot alcohol; on cooling, the new compound separated quite rapidly. It dissolves in warm water. The *o-toluidine* derivative, obtained by heating together equivalent quantities of the phenol and toluidine, consists of golden yellow plates, soluble in hot alcohol. It melts at 140° C. and solidifies at 115° C.

The *p-toluidine* compound separated from its alcoholic solution in reddish-yellow needles, quite soluble in water, and melting at 157° C. With *urea* the phenol does combine, but the union is evidently unstable, since by exposure to the air a gradual change in colour was perceptible. The *carbazol* compound consists of intensely red-coloured needles, melting at 121° C. It dissolves quite readily in alcohol. With *p-nitraniline* long needles were obtained. Their colour resembled that of chromic acid. It was rather difficult to obtain them pure. The *anthracene* derivative forms plates with an intense red colour. The union is not stable, and exposure to the air causes a gradual decomposition. The *morphine* compound is made up of bundles of needles, having a deep vermilion colour. It dissolves in alcohol, and melts at 97° C. The combination with *propylamine* is a yellow crystalline solid; that with *strychnine* consists of yellow nodular crystals, melting at 212° C.

The determination of the carbon and hydrogen in the aniline compound, and that of the nitrogen in the α-naphthylamine and *o*-toluidine derivatives, show that all the products described above are very probably combinations of a molecule of the chlordinitrophenol, with a like amount of the basic body.

I have further observed that dichlormononitrophenol, obtained in the nitration of dichlorsalicylic acid (*Am. Chem. Journal*, viii., 98), does not unite with aniline, so that it would seem that the acidic character of the phenol reached its limit with the dinitro-product; and that union with bases such as those given above, is not possible when but one NO_2 group is present.

The facts here communicated are to be regarded as preliminary to an investigation now going on, but which must shortly be suspended for some months.

* Read at the Meeting of the Chemical Section of the Franklin Institute, May 21, 1889.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1889.

Dr. W. J. RUSSELL, F.R.S., President, in the Chair.

MESSRS. James Hall, B.A., B.Sc., and J. W. Slater were formally admitted Fellows of the Society.

Certificates were read for the first time in favour of Messrs. Thomas William Dukes, Cape Town, South Africa; Theodore Francis Garrett, 36, Drakefell Road, St. Catherine's Park, Hatcham, S.E.; Eric Henry Jackson, B.Sc., Harefield, Morley Road, Southport: William Whitehouse, Myrtle Villa, Dixon's Green, Dudley.

The following were elected Fellows of the Society:—Edward Wightman Bell; William D. Cargill, B.Sc.; George William Howard; Frederick Charles Knight; Henry W. Morrow, B.S.; D. O'Mahoney; Benjamin Phillips; Robert Redwood; Emanuel Roberts; Robert M. W. Swan.

The following papers were read:—

62. "*Observations on the Melting-point of some Salicylic and Anisic Compounds.*" By W. H. PERKIN, Ph.D., F.R.S.

The author, after referring to his paper published in the Journal of the Society in 1867, in which methylated and ethylated salicyl aldehyds are described as nearly colourless fluids which do not solidify when cooled in a freezing mixture, and to the apparently contradictory results of Voswinckel (*Ber.*, 1882, 2024)—who states that methylated salicyl aldehyd is a solid melting at 35°—points out the curious fact that, although this latter aldehyd does not easily crystallise in a freezing mixture, it can be made to do so; the crystals, however, melt at about 2·7—3°. On evaporating an ethereal solution of the aldehyd, he obtained prismatic crystals, having the melting-point given by Voswinckel, and it was found that if the oily aldehyd be touched with one of these it immediately becomes a solid mass having a melting-point of 35°. On re-melting this solid, and then cooling in a freezing mixture, crystals melting at 2·7—3° can again be obtained. It is therefore established that methylated salicyl aldehyd forms crystals of two kinds, having melting-points differing by about 32°.

Ethylated salicyl aldehyd can also be made to crystallise; the crystals melt at about 6° or 7°.

Anisic aldehyd also crystallises when cooled; although a para-compound, it melts at a lower temperature than either modification of methyl salicyl aldehyd, viz., at 0·02°.

Ethylic anisate easily crystallises (m. p. = 7°), but ethylic methyl-salicylate has not as yet been obtained in a crystalline condition.

63. "*The Action of Propionyl and Butyryl Chloride on Phenol.*" By W. H. PERKIN, Ph.D., F.R.S.

In preparing phenyl propionate and butyrate by means of phenol and propionyl and butyryl chloride, the author has observed that secondary products are also formed,

which are proved to be new phenols containing acid radicles in place of hydrogen in the phenyl-group, viz., $C_3H_5O{\cdot}C_6H_4{\cdot}OH$, and $C_4H_7O{\cdot}C_6H_4{\cdot}OH$. They are both crystalline compounds, propionylphenol melting at 148·5°, butyrylphenol at 91°; they are soluble in ammonia solution.

Phenylic acetate, which has been previously described as an oil, was obtained in a crystallised condition; it melts at 20° and boils at 211° (corr.).

Phenylic butyrate, which has not been previously prepared, is an oil boiling at 227—228° (corr.).

64. "*The Nature of Solutions as Elucidated by a Study of their Freezing Temperatures.*" By S. U. PICKERING.

A series of determinations of the freezing temperatures of mixtures of sulphuric acid and water was undertaken in order to obtain further confirmation of the existence in solution of the various hydrates which had been indicated by the densities, heat of dissolution, heat capacity, and electric conductivity of these solutions, as well as to throw some light on Raoult's method of determining molecular weights.

The determinations with solutions containing over 4 per cent H_2SO_4 were attended with considerable difficulty, as the solution does not freeze, but one of its constituents crystallises out, the change being identical in nature with the crystallisation of a salt from a saturated solution; what has to be determined, therefore, is the temperature at which the given solution becomes saturated. This was done by cooling the liquid down until a good crop of crystals was obtained; it was then put in a vessel of water, and the rise of temperature noted at every half minute; the temperature at which the last crystals had disappeared was signalised by a sudden alteration in the rate of this rise.

The author has, so far, plotted the results only against percentage composition. The general results are represented by three independent curves, in which water, $H_2SO_4{\cdot}H_2O$, and H_2SO_4 itself are the substances which crystallise out.

The first of these curves is represented by an approximately straight line as far as 8 or 9 per cent H_2SO_4, falling at the rate of about 0·5° for every 1 per cent; it then curves rapidly downwards, the crystallising temperature of a 30 per cent solution being 36°; a little beyond this point it appears to become almost vertical. From 30 to 77 per cent no freezing-points have been attained. At this latter strength the crystallisation of the monohydrate begins. This crystallisation is represented by a curve with two branches, having its highest point at 84·5 per cent (the composition of $H_2SO_4{\cdot}H_2O$) and 8·5°, and falling away from this point on either side, at first gradually, and then abruptly. At about 94 per cent this curve meets that representing the crystallisation of H_2SO_4, the temperature being −31°; the H_2SO_4 curve rises from this point in an approximately straight line up to 100 per cent and 10·35°, when it turns abruptly down again in a curvilinear direction, the determinations having been extended as far as 101 per cent.

A closer inspection of these several curves shows that none of them are continuous, but that they are made up of separate curves or straight lines, which seem to be quite independent of each other, and show breaks of a most marked character, often corresponding to differences five or ten times greater than the experimental error. These breaks occur in every case at the same points as those observed by the author in the densities and other properties, and are of a very much more certain character than in any of the other cases. Of the 17 hydrates of sulphuric acid which he previously indicated, 12 are very satisfactorily confirmed by the present observations; the other five (H_2SO_4 with 2, 4, 5, 9, and 13 H_2O) would be shown only in that portion of the diagram where no freezing-points have yet been reached. In addition to this, there appear to be three other breaks, which the previous work would have been insufficient to show, at 98·7, 86, and 82·5 per cent, corresponding to—

$$12H_2SO_4{\cdot}H_2O,$$

$$7(H_2SO_4{\cdot}H_2O){\cdot}H_2SO_4,$$

and $7(H_2SO_4{\cdot}H_2O){\cdot}H_2O$, as well as a break at 100·7 per cent, representing $27H_2SO_4{\cdot}SO_3$, and at 100 per cent, or H_2SO_4 itself. It is especially noteworthy that the breaks at the extreme end of the curve corresponding to H_2SO_4 with 500, 1400, and 5000 H_2O have been fully confirmed.

The marked character of these breaks (which are apparent without any differentiation) leads to the hope that the method may be applicable in the case of solutions of organic liquids where other methods would fail.

Each of the three main curves which represent the general results tend downwards at an increasing rate as we pass from the highest points in them, and this tendency would also be exhibited if the results were plotted against molecular instead of percentage composition. This, the author shows, is what their character should be if hydrates were formed in solution, whereas on the physical theory of solution, they should tend downwards at a diminishing rate; so that the general form of the curves, independent of there being breaks in them, is conclusive in favour of the hydrate theory.

Passing on to the bearing of these results on Raoult's method, the author repeats his assertion that, at the best, this method could only give us the molecular weights of substances in the gaseous condition at the temperature of the determination, for in dilute solutions the molecules of the dissolved substance are as far removed from each other as they are when vaporised.

There are, however, no theoretical considerations which justify our regarding the molecular weight thus obtained in the same light as that obtained from vapour-densities. The vapour-density is a constant within experimental error throughout a very long range of conditions, whereas the lowering of the freezing-point could only be a constant on the supposition that dissolution is entirely physical and that the dissolved molecules act independently of the solvent. The present results show that it is not a constant, and that we have no grounds for supposing it to be such even with extremely dilute solutions. The irregularities and breaks which characterise the whole results have been traced back as far as a 0·1 per cent solution, and a further extension of the determinations, if possible, would simply reveal a continuation of these irregularities. On the other hand, it must be admitted, as, indeed, the practical results prove, that these irregularities would often lead to no great error in the molecular weight found, provided the solutions used are not too strong.

The author shows that such would be the case with the sulphuric acid curves, when the crystallisation of water is used to determine the molecular weight of H_2SO_4, or that of sulphuric acid to determine the molecular weight of H_2O. But the case is otherwise when we use the crystallisation of the monohydrate to determine the molecular weight of H_2SO_4 on the one hand, and H_2O on the other. Within 5 per cent of $H_2SO_4{\cdot}H_2O$ we should get results such as 18 for H_2SO_4 and 6 for H_2O. This shows that, although Raoult's method may give approximately correct results in many cases, we can never rely on it without performing an extensive series of experiments. There are no theoretical considerations which would lead us to suppose that it is reliable, and this investigation proves that each case has peculiarities of its own, which may lead to an entirely erroneous molecular weight.

65. "*Note on the Determination of the Molecular Weight of Substances in Solution, especially Colloids.*" By HENRY E. ARMSTRONG.

The fundamental conception underlying the now very general acceptation of the Raoult methods of determining molecular weight is undoubtedly the conception introduced by Van't Hoff that substances are present in dilute solutions in a state comparable with the gaseous state (cf. Ramsay, *Chem. Soc. Proc.*, 1889, p. 44). But in gases, even in the most imperfect, the individual molecules exercise a very slight mutual attractive influence; otherwise, in fact, the gaseous state could not subsist. When

liquefaction ensues, it would appear to be owing to, and to involve the exertion of, such mutual intermolecular attractions; and however continuous the states of gas and liquid may appear from a mathematical standpoint, the continuity would seem to be only that kind of continuity which is observed in dissociative changes generally. Although statistical analysis may support the conclusion that the gaseous state and that which obtains in a dilute solution are comparable, a consideration of the phenomena in the light of our knowledge of intermolecular relationships cannot at present be held to justify any such assumption; how can it be permissible, in fact, to compare the approximate truth of the laws of Boyle and Gay-Lussac with Raoult's if in solution an all-important part be played by a factor—the solvent—which, in the case of gases, may be left almost entirely out of consideration; and if water be not a neutral substance and the phenomena of dissolution are, as many believe, of a high order of complexity.

The regular and rational results which are obtained on applying the Raoult methods to dilute solutions of substances of known molecular weight are undoubtedly very striking and likely to carry conviction to many minds that the methods are of universal application; but other equally striking coincidences have been observed. Thus it is highly remarkable that the hydroxides generally—in dilute solutions be it observed—have the same heat of neutralisation. This illustration is of special moment, for if we consider the supposed interagents alone and disregard the solvent as a chemical agent, it is inconceivable that such should be the case; the result must be in some way a consequence of a higher law not yet clearly perceptible through the haze of complexity which so enshrouds the phenomena of chemical change in solution. It cannot be doubted that the constancy is conditioned by the presence of water in large relative quantity, as most irregular and dissimilar results are obtained if the comparison be made for any other than dilute solutions, just as in the case of the Raoult freezing method (cf. Beckmann, *Zeit. Phys. Chem.*, 1888, 638 and 715).

If the argument here advanced be admitted, it follows that not only the molecular weight of a substance but also its *specific effect* must be taken into account; and this is undoubtedly the case. It is well known that acids and metallic salts, and indeed electrolytes generally, give abnormal results; they produce too great an effect. Arrhenius has suggested that such compounds are present in solution in a more or less dissociated condition—dissociated into their "*ions;*" that, in fact, such solutions contain a greater number of active molecules than are usually supposed to be present. Allowing for this increase in a manner which he has pointed out, "normal" results are obtained in place of the impossibly low molecular weights which result from the direct reduction of the experimental values. But if we are to accept this view, we must admit that water is a neutral substance, and that it plays no active part in electrolysis; in other words, such a conclusion directly involves the acceptation of a particular hypothesis as to the nature of electrolysis. The arguments on which this hypothesis is based, however, are mostly cases of circular reasoning, and there are many facts which apparently cannot be satisfactorily accounted for by it (cf. *B. A. Report*, 1888, 356). The one argument in favour of the dissociation hypothesis which is generally regarded as all-sufficient—the argument originally advanced by Clausius, that any E.M.F., however small it may be, produces sensible electrolysis, is one of which it would be premature to accept any explanation as final in our entire ignorance of the inner mechanism of electrical actions—while the electric current is an unsolved mystery, as was happily observed by Professor Rowland in a recent lecture—especially as there are electricians who are of opinion that the Clausius hypothesis is not necessarily the only possible solution, although at present unable to suggest a more satisfactory one. But not only is the explanation of electrolysis which is usually given of a purely "mechanical" nature, and incompatible, therefore, with the view that the solvent plays an active part; it is open also to the objection that in framing it attention has been paid too exclusively to a certain limited number of phenomena, and that the bearing of the facts of chemistry generally as these present themselves to the mind of the chemist has been insufficiently considered. It is probable that this will soon cease to be the case, as signs are not wanting that it will ere long be recognised that chemical changes are essentially electrolytic phenomena, and that we may expect to witness the rehabilitation of Faraday's view of 1834 of "the identity of the force constituting the voltaic current or electrolytic agent with that which holds the elements of electrolytes together, or, in other words, with chemical affinity."

Although it may be urged that the method which Arrhenius has introduced of correcting the results obtained in the case of electrolytes is based on an incorrect interpretation of the phenomena, it does not follow that his method is necessarily a faulty one: on the contrary. Practically the method involves nothing more than the recognition of the fact that it is possible to determine with a close approach to accuracy, and to allow for, the *specific effect* which a compound exercises. This would seem to be the case. Thus Ostwald's experiments show that in the case of acids, for example, in seeking to determine the order of activity in which these may be arranged, practically the same result is arrived at, the order deduced being very similar when very diverse properties are made the subject of study. Molecular weight does not come into evidence as a determining cause of position in such a series, compounds such as hydrogen chloride, bromide, and iodide occurring together and almost at the head of the scale of activity, while hydrogen fluoride is found low down in the series. The compounds in such a series afford "abnormal" values when examined by the Raoult methods in dilute solutions owing to their exercising a greater effect than is produced by compounds which give "normal" values; the extent to which the effect produced is in excess depends on the position in the series, and if proper allowance be made on this assumption a "normal" value is necessarily obtained, *i.e.*, a value consonant with the view which on general grounds we are led to form as to what would be the composition of the molecule of the substance if it were obtained in the gaseous state. But it has yet to be proved that such "corrected normal" values, and those directly found for neutral compounds which can be gasified, uniformly represent the true molecular weights of the dissolved substances, and not merely the weights of their fundamental molecules (cf. *Proceedings*, 1889, 42).

Whereas in dilute solutions an excessive effect is often produced which would lead to the molecular weight being under-estimated if the result were at once accepted, in the case of concentrated solutions a contrary result is frequently encountered, corresponding to more or less exaggerated estimates of the molecular weight; thus the effect produced by alcohol, for example, in a 32·5 per cent solution is such as apparently to correspond to a molecular weight of 318 (Beckmann). It is not difficult to explain this result on the mechanical hypothesis of the nature of solutions, and still less difficult on the assumption that dissolution is in the main a chemical process: inasmuch as in concentrated solutions less opportunity is given for the molecules of the dissolved substance individually to exercise their specific heat; inasmuch as molecular aggregates are more likely to persist; and inasmuch as the solvent may consist no longer of the substance ostensibly employed as solvent, but in part, at least, of a compound of solvent and dissolved substance. The reduction of the specific effect, and the consequent exaggeration of the molecular weight in the cases here contemplated, may be said to be due to inter- if not to extra molecular compensation.

But it is also conceivable that intra-molecular compensation may take place, and that there may be compounds, the existence of which is not to be foreseen on the dissociation hypothesis, which exercise not an excessive but an inferior effect. The molecular weight of such compounds would necessarily be over-estimated by the application of the Raoult methods. Benzene and thiophen may be cited as mere illustrations of what is meant by internal compensation; benzene, it is well known, does not manifest the activity of a "triethylenic" compound, and evidently, in some manner not clearly understood, the six "surplus" affinities of the six carbon atoms internally neutralise or compensate each other; in thiophen the sulphur appears to function only as a dyad, manifesting no tendency whatever to exhibit a higher valency in the manner so characteristic of sulphur in open chain compounds: the inclusion of the sulphur in the chain in this case, therefore, involves a marked diminution in its activity.

It may be suggested that probably colloids generally are compounds of inferior activity, such as are contemplated on the view here put forward. It is well known that they diffuse with extreme slowness (*cf. Nature*, xxxv., 598), and they are as a class very inert substances, the vapour-pressures of their aqueous solutions, for example, being almost if not the same as those of water alone at the same temperatures. The results recently brought forward by Brown and Morris for carbohydrates are of great interest, but it may be doubted whether they do more than confirm the views previously held with regard to the relative complexity of the several compounds. The same remark applies to the observations of Gladstone and Hibbert on caoutchouc. The fundamental molecule of a glucose must contain at least 6 carbon atoms, and that of a saccharon (any member of the cane-sugar group) 12; that of an amylin (or dextrin) therefore most probably contains at least 24 carbon atoms. A variety of *amyloins* might well result from the conjunction of amylon (maltose) and amylin molecules in various proportions: maltodextrin,—

$$C_{12}H_{22}O_{11}\cdot 2C_{12}H_{20}O_{12} = C_{12}H_{22}O_{11}\cdot C_{24}H_{40}O_{20};$$

inulin,—

$$2C_{12}H_{22}O_{11}\cdot 4C_{12}H_{20}O_{10} = 2C_{12}H_{22}O_{11}\cdot 2C_{24}H_{40}O_{20};$$

and amylodextrin,—

$$C_{12}H_{12}O_{11}\cdot 6C_{12}H_{20}O_{10} = C_{12}H_{22}O_{11}\cdot 3C_{24}H_{40}O_{20},$$

representing these by the formula assigned to them by Brown and Morris, are apparently such compounds. By duplication of the molecule and withdrawal of the elements of water from such amyloins, "higher dextrins" might be formed which would still be compounds of moderate molecular weight; and even simpler compounds would result if the amyloins were merely to lose the elements of water. Compounds thus formed would undoubtedly be less active than the parent carbohydrates, owing to the "cancelling" of the hydroxyl-groups; and it may well be that they would exercise an inferior effect in solution, and one such as is observed in the case of colloids.

It is undoubted that by the application of the Raoult methods a number of most interesting facts have been elucidated, which it is impossible and unnecessary to deny, but it is equally certain that we are only called on to make a rational use of them, and that slavish submission to the facts cannot be demanded. Those who directly accept the conclusions which are drawn, perhaps, have hardly realised what is involved, viz., adherence to the view that in a dilute aqueous solution of hydrogen chloride, for example as much as 90 per cent of the chloride is present, not as such, but in the form of *free hydrogen and chlorine atoms:* such a conclusion may enable certain mathematical problems to be solved in an apparently satisfactory manner, but it is hardly one which a chemist's common sense would lead him to accept orthwith, in the absence of any explanation accounting for so extraordinary a difference between a dissolved substance at a low temperature and the same substance in the gaseous state at a high temperature. Attention may also be directed to the contradiction involved in the assumption that hydrogen chloride, although not appreciably dissociated when heated alone at 1500° in porcelain (Crafts and Meier) undergoes almost complete dissociation when dissolved in water, whereas nitrogen peroxide, according to Ramsay's experiments, exists in solution as N_2O_4, notwithstanding that it cannot be gasified unchanged, and is almost entirely resolved into NO_2 molecules at a temperature of about 200°.

Discussion.

Dr. Gladstone defended Raoult's freezing method, relying on the numerous coincidences between its indications and those afforded by vapour-density determinations. In illustration he referred to the polymeric C_5H_8 hydrocarbons. Mr. Hibbert and he had found that each of these, when dissolved in benzene, gave a freezing-point indicating an analogous molecular composition in the gaseous and dissolved condition. The conclusion from the small lowering produced by colloids that they have a very complex molecule is only in accordance with what has been long believed on chemical grounds. No doubt there are discrepancies and difficulties; but a careful consideration of these must serve to improve our knowledge of chemical and physical theory.

Mr. Hibbert said, that in applying Raoult's method, he had found it advantageous to surround the freezing vessel with an air chamber. The freezing-point was then more definite.

The contention of Dr. Armstrong against the applicability of Raoult's method to colloid substances was based on objections to the dissociation theory of electrolysis. It might be true that the only argument in favour of that theory was the fact that the smallest electromotive force was able to produce decomposition in an electrolyte, but the argument was a very strong one, and commanded the assent of nearly every physicist in Europe. With reference to the effect of colloids on boiling-point, &c., the question was whether they did or did not produce a real alteration. Recent researches seemed in favour of a positive result.

66. "*The Correspondence between the Magnetic Rotation and the Refraction and Dispersion of Light by Compounds containing Nitrogen.*" By J. H. Gladstone, Ph.D., F.R.S., and W. H. Perkin, Ph.D., F.R.S.

The substances containing nitrogen, the magnetic rotation of which was described in Dr. Perkin's recent paper, have been examined by Dr. Gladstone with reference to their refraction and dispersion. The result is given in a table in which the molecular magnetic rotation, molecular refraction, and molecular dispersion for 41 substances are placed in parallel columns with a view of drawing attention to the general correspondence that exists between these three different properties of the substances in question; a correspondence that points to some connection between the rotation of the polarised ray under magnetic influence and the retardation of the rays of light in passing through a material substance. Each property is governed by the following primary law. The molecular magnetic rotation, refraction, or dispersion of a compound body is the sum of the atomic magnetic rotation, refraction, or dispersion of its constituents. The values which have been deduced under this primary law are, however, subject to large modifications dependent upon differences in the structure of the compound.

The paper shows that when a change occurs in one property, it is noticeable also in the other two, and these changes are in the same direction, though not to the same extent; in fact, the variations in the magnetic rotation are usually greater than those in the dispersion, and these again are much more marked than in the refraction.

Eight sets of comparisons are given, each showing the correspondence in a different way:—

1. Compound ammonias. Ethylamines and propylamines, showing for each additional substitution a continuous augmentation of the value,

2. Hydrochlorides of the ethylamines, showing for each substitution a value smaller than the normal.

3. Methylanilines, showing a greatly increased value for CH_2.

4. Unsaturated compounds, allylamine, pyridine, and aniline, showing a great increase upon the values for saturated compounds.

5. Propylamine compared with propionitril and trimethylene cyanide, showing two different values for nitrogen.

6. Nitric ethers, showing normal values for each CH_2, except the first.

7. Isobutyl nitrite and nitrate, showing the diminution of the nitrogen value with change of valency.

8. Acids and their ammonium salts, showing a superior value for acids in aqueous solution, and its continuance or partial disappearance on combination with nitrogen bases.

Apparent exceptions are mentioned, but the following is the general conclusion :—

It may be laid down as generally if not always true, that where there is a departure from the normal values in regard to one or other of these properties, it is to be found in the other two. The different properties are evidently similarly affected by change in chemical constitution. The general drift of the old comparison appears to lead irresistibly to the conclusion that we have here another close relationship between electromagnetism and the velocity of light.

(To be continued).

CORRESPONDENCE.

THIOCAMF.

To the Editor of the Chemical News.

Sir,—In reference to Mr. T. Bruce Warren's letter in the Chemical News, vol. lx., p. 36, allow me to point out that our registered name "Thiocamf" applies specially to a disinfectant compound in which the sulphur dioxide and camphor liquid is the solvent for other powerful disinfectants.—I am, &c.,

The Secretary,
Thiocamf Disinfectant Co.

Thiocamf Disinfectant Company,
5, Lower Merrion Street. Dublin,
July 22, 1889.

The Detection of Sugar in the Commercial Extract of Logwood. — Otto Schweissinger (*Pharm. Central-halle*).—From 2 to 5 grms. of the extract are dissolved in 50 c.c. water, mixed with 10 c.c. basic lead acetate, well shaken, and, after standing for a short time, poured upon a dry filter. So much of the liquid runs through that it can be at once polarised in a tube 100 m.m. in length. Filtrates from pure extracts deflect the plane of polarisation not at all or but little, certainly not to the right. The entire filtrate (25 to 30 c.c.) is mixed with so much lead chloride that the lead is precipitated as chloride and about 0·5 grm. hydrochloric acid remains in excess. The acid liquid is heated in a reflux condenser for half an hour and let cool. The crystals of lead chloride are disregarded and the liquid is neutralised with sodium carbonate, filtered, and titrated with Fehling's liquid. Two pure samples, when thus treated, showed no sugar, three suspicious ones respectively 6, 7, and 8 per cent, and a grossly adulterated sample 20 per cent.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 2, July 8, 1889.

Solubility of Carbonic Acid Gas in Chloroform.—M. Woukoloff.—Carbonic acid, when dissolving in chloroform at 13°, does not follow strictly the law of Dalton, but the deviations are very small, as we have also seen for carbon disulphide.

Solidification of Nitrous Acid.—Fl. Birhans.—To solidify anhydrous nitrous acid, though still containing small quantities of hyponitric acid, there is required a temperature of −52° to −54°, obtained by the evaporation of methyl chloride in a current of dry air. To obtain anhydrous nitrous acid free from hyponitric acid, the author has operated similarly to Fritsche, but at a lower temperature. It forms a fine blue liquid, which was solidified only by the cold produced by a mixture of methyl chloride and carbonic acid in the flocculent state. This mixture, according to the experiments of MM. Cailletet and Colardeau, lowers the temperature to −82°.

On the Barium Cobaltites, and on the Existence of a Cobalt Dioxide having an Acid Function.—G. Rousseau.—The author's experiments show the existence of a cobaltous acid analogous to manganous acid, but feebler. The maximum stability of barium manganite lies about 1100°. The compound is dissociated either at higher or lower temperatures.

A Copper Oxybromide, analogous to Altacamite.—Et. Brun.—A solution of potassium bromide, saturated in the cold with cuprous bromide, deposits, when left in contact with the air, a precipitate which, after being freed by decantation from the supernatant liquid, and being repeatedly washed with a solution of potassium bromide, appears in the form of small deep green crystals, insoluble in water, but soluble in dilute acids and in ammonia. At 240° to 250° this compound is entirely destroyed, and the residue, on treatment with water, gives off copper chloride, which dissolves, whilst copper oxide remains as a black powder.

New Derivatives of Camphor.—M. Haller.—This memoir is not susceptible of useful abridgment.

On the Dioxyphosphinic Acids. — J. Ville.— The aldehyds unite directly with hypophosphorous acid and yield trivalent and monobasic acids. These acids have no reductive action upon ammoniacal silver nitrate and upon copper sulphate; they have a tendency to become split up, setting at liberty the aldehyd from which they are derived.

Researches on the Purple produced by Purpura Lapillus.— Augustin Letellier. — This mollusk is very common on the shores of Bretagne, and was formerly used by the Bretons in dyeing. The colour is generated in a yellowish white band. The purple is, in fact, produced by three substances, one of them yellow and not photogenic, whilst the two others turn quickly to a blue and a carmine red under the influence of the sun's rays. The yellow substance forms crystals similar to those of uric acid. The substance is soluble in potassa, whence it may be precipitated by weak acids. The two photogenic substances are the one apple-green and the other ash-green. The crystals of the former have the appearance of magenta; light quickly renders them opaque and deep blue. They dissolve sparingly in water but readily in chloroform and in petroleum ether. The crystals of the third body are very soluble in water. They become red, violet, or carmine on exposure to light, according to their degree of purity. To prepare even a very small

quantity of these three bodies the bands must be detached from several hundred specimens of *Purpura* dried at the common temperature in a vacuum over sulphuric acid. When dried they are powdered, treated with ether, which is let evaporate, and the residue is taken up in potassa, which dissolves the fats and the yellow matter. The whole is filtered. The filtrate, on the addition of acetic acid, deposits the yellow matter. The green residue on the filter is treated with chloroform, which dissolves the ash-green substance more readily than the apple-green. If petroleum ether is used the apple-green crystals dissolve more rapidly. All these operations must take place in the dark. When once formed the purple is an impalpable powder, insoluble in the ordinary solvents. Nitric acid and chlorine-water destroy it; sulphuric acid converts it into an emerald green substance, which, on the addition of water, becomes an indigo-blue liquid, but in time the matter becomes carbonised. The action of light upon the purple matter suspended in chloroform is curious. It extinguishes the less refrangible red rays, absorbs the yellow, the most refrangible part of the blue, all the indigo, and all the violet. We have a continuous spectrum formed of a dirty orange-red band, contiguous by irradiation with a broad green band edged with blue. The yellow is so well absorbed that it is not perceived. The only radiations which pass through are those comprised between 720 and 613, 535 and 490. The purple seems to take its rise by a process of reduction. The purpurigenous matter, if treated with oxygenated water, hypochlorous acid, or potassium dichromate, remains intact, but in presence of sodium amalgam it turns to a reddish purple.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 2.

Determination of Theine in the Teas of Comerce.m—Hilger (*Archiv der Pharmacie*) exhausts 10 to 20 grms. of tea repeatedly with boiling water, precipitates the filtered extract with basic lead acetate, avoiding a large excess, filters off the precipitate, washes with hot water, and decomposes with hydrogen sulphide. The filtrate is evaporated to dryness after the addition of wash-sand and a little lime or magnesia, and the residue is extracted perfectly with boiling chloroform in Soxhlet's apparatus. This extract yields a slightly coloured residue, which, after drying for three hours at 100°, is weighed, and may be obtained perfectly colourless by re-crystallisation from alcohol or boiling water.

Determination of Uric Acid.— A. Hermann (*Zeit. Physiolog. Chemie*) has examined Haycraft's method, and concludes that, though the results are too high, it may be useful in clinical examinations.

The Spectrum of Methæmoglobine.— H. Bertin-Sans.—From the *Comptes Rendus*.

The Spectrum of Reduced Hæmoglobine.—L. Hermann (*Pflüger's Archiv*).—In the broad absorption-band between D and E near the edge towards the red there is a narrow rather lighter interval. Hence the absorption-band in a rather narrow spectrum appears to consist of a narrow absorption stripe near the line D and a broad one extending towards E.

The Spectroscopic Demonstration of Traces of Blood in Urine and in Other Liquids.—C. H. Wolff (*Pharm. Central-halle*) puts 30 to 60 c.c. of the urine in question in a capacious test-tube with one-tenth its volume of a three per cent solution of zinc acetate and heats it in the water-bath until the precipitate collects together and settles so far that the supernatant liquid can be decanted clear. The deposit is collected upon a small filter, washed, and covered with a few c.c. ammonia. The precipitate dissolves and the solution is let run into a test-tube 10 c.m. in length and 12 m.m. in width and made up to 4 to 5 c.c. by washing the filter. The filtrate is covered with a few c.c. of benzine, to exclude air, and mixed with 2 drops of a solution of ferrous sulphate containing tartaric acid (1 part each of tartaric acid and ferrous sulphate in 10 parts water), whereby the hæmatine is reduced and may be examined with the spectroscope. The characteristic absorption-band in the green,—

$$\alpha = \lambda\, 564—547,$$

can be seen even in the greatest dilution.

Densimetric Determination of Albumen in Animal Fluids. — Huppert and Záhor have examined the applicability of this procedure as proposed by Bornhardt.

MISCELLANEOUS.

London Sewage.—In view of the difficult question of the disposal of London sewage receiving the attention of the London County Council shortly, Sir H. Roscoe, M.P., has issued a statement of the position of affairs. Sir Henry has come to the conclusion that the proposal of the Board of Works for the disposal of the sewage was based on false principles—first, as regards the addition of lime and iron in the proportions recommended; second, as regards the addition of manganate of soda to the effluent, after precipitation, in the quantities suggested; third, as regards the formation of underground settling tanks at Barking and Crossness; fourth, as regards pumping the sludge into tank steamers and sending it out to sea. On this £1,013,786 had been spent from 1884—88 inclusive. Sir H. Roscoe suggests that an engineer of high eminence, and a chemist of like position, should at once be appointed to reconsider the whole question.— *Gravesend and Dartford Reporter.*

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Chemical Manufacturers.—J. M. wishes to learn the publisher of a work containing a list of chemical manufacturers.

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THE CHEMICAL NEWS.

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ROYAL COLLEGE OF SCIENCE

ON

RECENT RESEARCHES ON THE RARE EARTHS AS INTERPRETED BY THE SPECTROSCOPE.*

By WILLIAM CROOKES, F.R.S., &c.

Continued from p. 41).

The Yttrium Group.

Yttrium—the old yttrium—proves now to be not a simple element, but a highly complex substance. I have come to the conclusion that it may be split up certainly into five and probably into six constituents. Its phosphorescence spectrum is shown in Fig. 16, and the different bands are designated by certain letters. Fig. 17 shows the simple spectra of the separate components into which yttria can be separated by fractionation. If we take these constituents in the order of their approximate basicity — the chemical analogue of refrangibility — the lowest of these constituents gives a deep blue band, Gα; then follows a strong citron band, Gδ, which increases in sharpness until it may be called a line; then a red band, Gζ; then a deeper red band, Gη; and lastly a close pair of greenish blue lines, Gβ. Following these are frequently seen Gε, Gγ, and Gθ, the yellow, green, and red components of samarium, Fig. 19.

As the result of many years' work and several thousand fractionations of old yttria, I exhibit the series of 19 phosphorescence spectra shown on Diagram 28. The centre spectrum, marked J, is approximately that given by the crude earth, although this differs slightly according to the mineral from which it is extracted. After a time, fractionation splits the earth J into two earths, I and K, giving slightly different spectra. Fractionating I gives H and J, whilst K on fractionation yields J and L. The state of separation to which the meta-elements of the samarskite earths may be brought after many years' work is seen by the series of 19 spectra selected to illustrate the progress of the work. It must not, however, be thought that there is so great a difference between any two adjacent spectra as is here shown. To make the diagram more accurately represent what actually occurs in the laboratory it would be necessary to place between each of these 19 spectra about 1000 intermediate spectra.

Beginning at the extreme red it will be seen that a strong band at λ 647 ($1/\lambda^2$ 239) is of maximum intensity from G to K, when it rapidly disappears and is not seen beyond C and N. The meta-element giving this band I have called Gη. The next band in the red λ 639 ($1/\lambda^2$ 245), is at its maximum at A or even above, while it fades out between K and L. The next band at λ 619 ($1/\lambda^2$ 261) has its maximum between I and O, fading out rapidly below, but being more persistent above. The meta-element to which this band is due I have called Gζ. I next come to an extremely sharp band at λ 609 ($1/\lambda^2$ 269), which appears to belong to an earth absent in gadolinite, and present in samarskite and a few other minerals. Its greatest brilliancy is between E and K, dying away rapidly on either side. This meta-element I have called Sδ. A double orange band follows, and there are indications that its two components are separable, although they must be very closely associated. The maximum brightness of the first component, λ 603 ($1/\lambda^2$ 275), extends from O to the top of the diagram. The second component, λ 597 ($1/\lambda^2$ 280), begins to lose brilliancy about G, and, like its companion, is at its greatest brightness at the highest spectrum shown on the diagram. This band has been almost isolated in a specimen of crude lanthana. I have called its meta-element Gε.

The next band in order is the citron or Gδ band, λ 574 ($1/\lambda^2$ 303·5), the most prominent in the spectrum of old yttrium. This band extends with almost undiminished sharpness and brilliancy from G to S; above G it fades out rapidly, and from D upwards it is absent. Following the citron band is a double green band. This, like the orange band just described, is separable into two components. The first, at λ 568 ($1/\lambda^2$ 310), is almost absent in A, attains its maximum in about D, and fades out entirely at K. The second component of this green pair, λ 563 ($1/\lambda^2$ 315), is at its maximum at A and above, and extends only to H. The meta-element giving rise to this pair I have called Gγ. Next in order comes a pair of bright green bands. The two components λ 550, 541 ($1/\lambda^2$ 331, 342) have not yet shown signs of dividing. The first appearance of this double band is at B, it attains its maximum at about E, and continues with almost undiminished brightness to Q. The body giving this double green band is the most persistent of all the meta-elements of these earths. I have provisionally called it Gβ.

After a dark interval a broad, hazy, double blue band is seen, having its centre at λ 482 ($1/\lambda^2$ 430·5). This band, first appearing at about F, increases in brightness down to the last fraction at S. Its meta-element is called Gα. Lastly, at λ 456 ($1/\lambda^2$ 481), is seen a deep violet band, coming in first at Q, and getting brighter as we get lower down the fractionations. This band is of extraordinary brilliancy in some samples of ytterbia, but as it is absent in a specimen of ytterbia from Nilson, said by him to be perfectly pure, it is probably due to some other new body which I have therefore named provisionally Sγ.

Although, for economy of space, it is inconvenient to represent a longer series than is here shown, my fractionations have been pushed far beyond the limits shown on the diagram. Fractions above A and below S give ample evidence that the process of differentiation has not reached its utmost limit.

On the left of the diagram, Fig. 28, I have attached chemical symbols to some of the spectra. Thus the top spectrum, A, is the one shown by samarium. At D is the spectrum given by Marignac's Yα or gadolinium. At H is seen the spectrum of mosandrum, and at L is shown the spectrum given by what would ordinarily be called pure yttrium. A study of this diagram will, I think, convince any impartial observer that the lessons it conveys fully bear out my contention that samarium, gadolinium, mosandrum, and yttrium, are not actual chemical elements, but are compounded of certain simpler bodies which may conveniently be called "meta-elements."

A possible explanation of the existence and nature of the new bodies into which "old yttrium" has been split up, and of parallel cases which will doubtless be found on closer examination, is this. Our notions of a chemical element must be enlarged; hitherto the elemental molecule has been regarded as an aggregate of two or more atoms, and no account has been taken of the manner in which these atoms have been agglomerated. The structure of a chemical element is certainly more complicated than has hitherto been supposed. We may reasonably suspect that between the molecules we are accustomed to deal with in chemical reactions, and the component or ultimate atoms, there intervene sub-molecules, sub-aggregates of atoms, or meta-elements, differing from each other according to the position they occupy in the very complex structure known as "old yttrium."

The arguments in favour of the different theories are

* Address delivered by the President of the Chemical Society at the Annual General Meeting, March 21st, 1889.

as yet not unequally balanced. But the assumption of compound molecules will perhaps account for the facts, and thus legitimate itself as a good working hypothesis, whilst it does not seem so bold an alternative as the assumption of eight or nine new elements.

The history of the examination of the rare earths and of its results would lack completeness and intelligibility did I not refer to the views taken by my distinguished friend M. Lecoq de Boisbaudran.

In a communication to the Academy of Sciences this eminent chemist says (*Compt. Rend.*, c., 1437): "It is a singular fact that the position of the phosphorescence bands observed by Mr. Crookes with very pure compounds of yttrium are sufficiently near those which I, on my part, have obtained with the hydrochloric solutions of earths separated as far as possible from yttria, chemically as well as spectroscopically. My reversion spectrum cannot, I think, be attributed to yttrium, for on the one hand it is seen *brilliantly* with products which give no trace of yttrium rays with the direct spark, and on the other hand, I have found it impossible to obtain it sharply from certain earths extremely rich in yttria."

M. de Boisbaudran further states in a note:—"This spectrum (*i.e.*, the one which he had just described) is now recognised as being identical with that which is ascribed to pure yttria by Mr. Crookes, and which this *savant* obtained under experimental conditions very different from mine. Nevertheless, my latest observations, as well as earlier ones, lead to the conclusion that yttria is not the cause of the spectrum bands observed. In my fractionations the phosphorescence spectrum gradually gets weaker as I advance towards the yttria end. With almost pure yttria the phosphorescent bands show themselves faintly or not at all, whilst they are brilliant with the earths which do not give by the direct spark the rays of yttrium to any appreciable extent."

It will, I think, appear that the issue between myself and M. de Boisbaudran turns on the question: What is yttria? To what substance can this name be legitimately given? A short time ago the name conveyed to all chemists only one meaning, perfectly definite and undisputed. I have received specimens of yttria from M. de Marignac, considered by him to be purer than any which had ever been previously prepared; from Professor Clève (called by him *purissimum*); and from M. de Boisbaudran, which he pronounces to be yttria "scarcely soiled by traces of other earths." Along with these I have specimens prepared by myself and purified up to the highest point known. A very short time ago every living chemist would have called these samples "yttria." Moreover, they all give my phosphorescence spectrum *in vacuo* with such intensity that such phosphorescence cannot be rationally ascribed to slight traces of impurities.

This substance, like other chemists, I formerly called "yttria," but since its complex nature has been ascertained I speak of it as "*old* yttria."

M. de Boisbaudran, however, inadvertently uses the word in a manner not quite free from ambiguity. By "yttria," I repeat that I mean now, and have always meant, the yttria of Clève, of Marignac, and of all chemists up to the beginning of the year 1886, the yttria whose metallic base has the approximate atomic weight of 89. M. de Boisbaudran at one time writes as if our meanings were identical: "It is certain," he says, "that my earth, very rich in yttria, gives a beautiful spectrum in the vacuum tube." Again he informs me, "M. Becquerel has recently examined my earths A and B in ultra-violet light, and has obtained results analogous to yours; that is to say, the earth rich in yttria has generally shone brighter than the other." The "earth A" here spoken of gives my phosphorescent spectrum with wonderful brilliancy, and is the one described above by M. de Boisbaudran as "yttria scarcely soiled by traces of other earths." This yttria, my distinguished friend goes on to say, "is the same as that of Clève and Marignac, varying only in slight impurities, Marignac's being perhaps the purer." So far then we agree in the meaning to be attached to the word "yttria."

But at other times M. de Boisbaudran gives the name "yttria" to an earth of quite distinct properties, to an earth he has obtained in most minute quantities after months of reiterated fractionation, which gives *no* spectrum in the vacuum tube. Here, therefore, we have the name "yttria" applied to two distinct substances, the one giving a brilliant phosphorescence spectrum, and the other giving none at all, surely a misleading ambiguity. Moreover, I am constrained to question the propriety of my friend's use of the designation "yttria" in the latter sense. Quite recently (*Compt. Rend.*, cviii., 166, January 28, 1889) M. de Boisbaudran has defined his "yttria" as an earth, whether simple or complex, having a characteristic spark spectrum, but not giving a phosphorescence spectrum in the radiant matter tube or by his process of reversion, and having an atomic weight of nearly 89 for its metal.

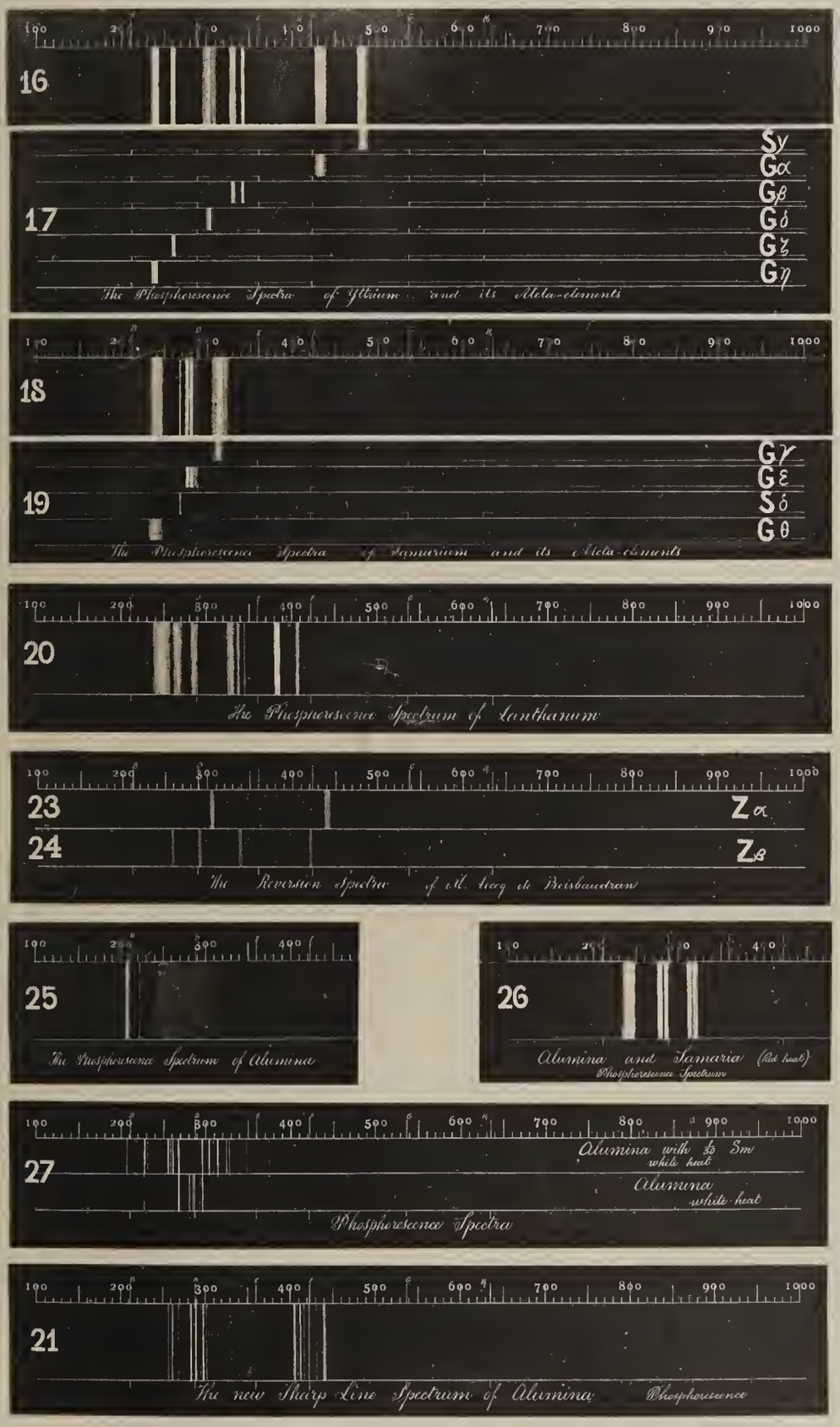
Why should this non-phosphorescent earth deserve the name of elemental yttria? Why may we not just as well allot the name to some one or other of the phosphorescing earths which M. de Boisbaudran brands as impurities? It seems to me that to refine away the most characteristic attributes of a body, to call the *caput mortuum* by the original name, and pronounce everything else as "impurity," is a departure from the recognised principles of scientific reasoning and practice which it is a duty to protest against.

I have just mentioned that the earth heretofore called yttria and supposed to be simple has been split up into a number of simpler bodies. Now these constituents of the old yttria are not *impurities* in yttria any more than praseodymium and neodymium are impurities in didymium. They proceed from a real splitting up of the yttrium molecule into its components, and when this process is completed the old "yttria" has disappeared. If these newly discovered components on further examination should be found worthy to take the rank of elements, I think as first discoverer, I am entitled by the custom prevailing among men of science, to name them. For the present, and until their investigation is more advanced, I designate them by provisional symbols. One of the most distinct characteristics of "old yttria" is its very definite spark spectrum. To which of its components this spark spectrum belongs I am not yet able to say. It is possible that the particular component to which the spark spectrum is due yields no phosphorescent spectrum. It is also possible that the spark spectrum, like "old yttria," may prove to be compound, and then the well-known lines it contains will have to be shared between two or more of the newly-discovered bodies. I wish emphatically to re-state that at present no single component of old yttria can lawfully lay claim to what may be called the paternal name; and it seems to me that in the present state of the question no one is entitled to call one of the new bodies "yttria," and to characterise the remainder as impurities.

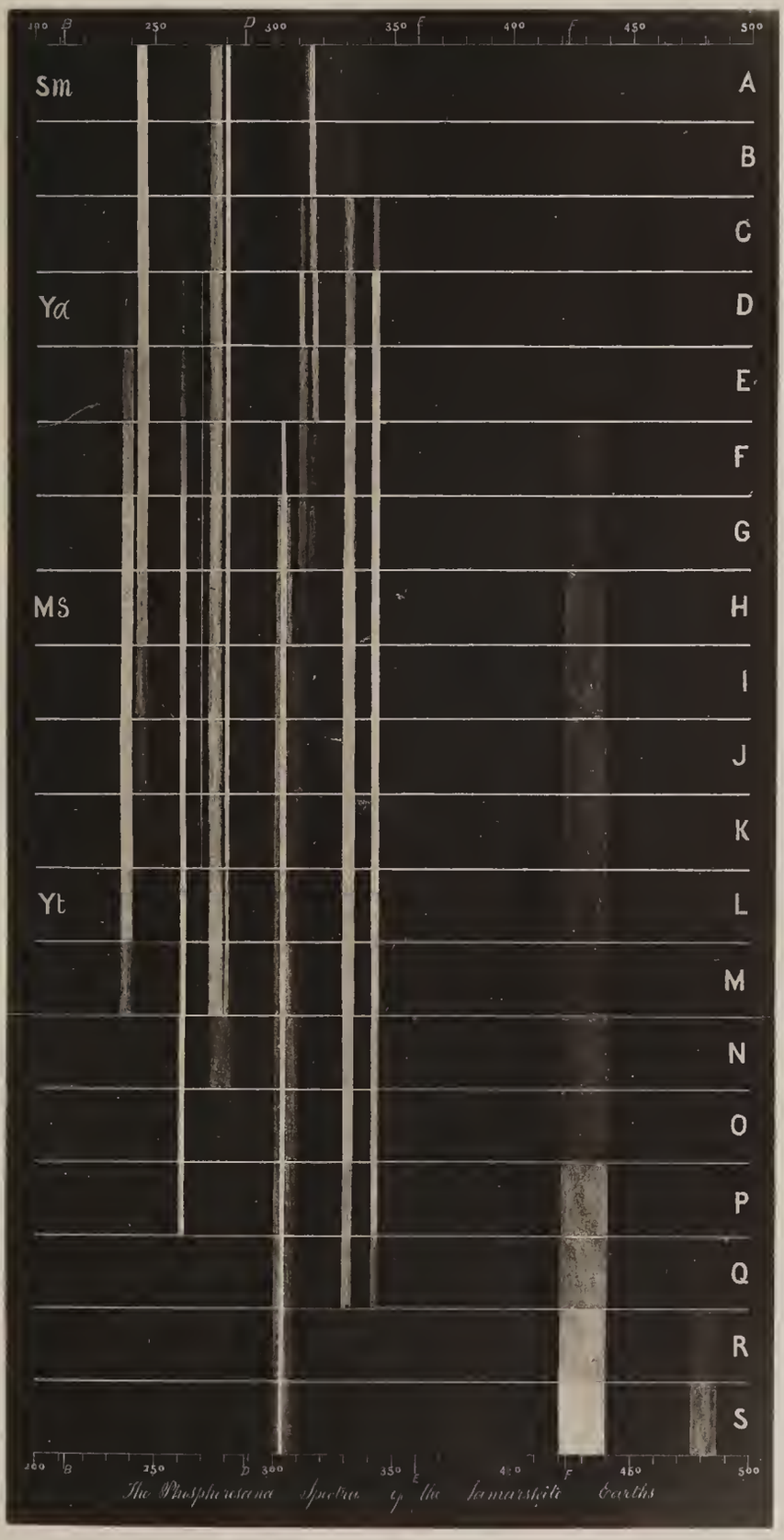
I regret to add that a misunderstanding exists between M. de Boisbaudran and myself. In a memoir presented to the Academy of Sciences on January 28th of the present year my distinguished colleague shows he completely misapprehends my position, and he so far misinterprets me as to make me say that the gadolinia or Yα of M. de Marignac is a mixture of 61 parts of yttria and 39 parts of samaria!

But what is the fact? So far back as June 9th, 1886, I put it on record (*Proc. Roy. Soc.*, xl., 502) that "Yα is composed of the following band-forming bodies:—λ [541—549], [564], [597], [609], [619], together with a little samarium. Calling samarium an impurity, it is thus seen that gadolinium is composed of at least four simple bodies."

Again in a paper entitled "What is Yttria?" I wrote (Chem. News, liv., 39, July 23, 1886)—



SPECTROSCOPIC RESEARCHES ON THE RARE EARTHS.
W. CROOKES.



SPECTROSCOPIC RESEARCHES ON THE RARE EARTHS.

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"Gadolinium is composed of at least four simpler bodies, Gβ, Gγ, Sδ, and Gζ; the pair of green lines [λ 541 and λ 449, mean 545], being the strongest feature in its spectrum, may be characteristic of gadolinium."

"M. de Boisbaudran says:—'Mr. Crookes appears to attribute to gadolinium the double green band.' This is scarcely accurate; I did not ascribe the double green band to gadolinium, but finding by my test that the *so-called* gadolinium was a compound body, the earth Gβ being its strongest component, I proposed to attach the name of gadolinium to Gβ rather than give it a new name, and thus multiply names unnecessarily."

Thus in 1886 I corrected the error which M. de Boisbaudran now repeats.

Again, I said that the work of fractionating this mixture, "*for its completion*, would occupy a space of time in comparison with which the life of man is all too brief"—a statement transformed into the assertion that to separate yttria and samaria—a relatively easy task—would take more than a life-time.

M. de Boisbaudran's misconception is the more striking since in a foot-note he gives correctly my very words from my "Address to the Chemical Section of the British Association," in 1886, and from the "Genesis of the Elements." How he can have mistaken my meaning is a mystery, as he is an excellent English scholar. Certainly any reader of the *Comptes Rendus* who understands English will at once see that there is no foundation for M. de Boisbaudran's criticism.

(To be continued).

ON ALLOTROPIC FORMS OF SILVER.*

By M. CAREY LEA, Philadelphia.

(Concluded from p. 45).

B. *Insoluble Form of the Foregoing.*

THE solution of the blue product just described is influenced in a remarkable way by the addition of almost any neutral substance. So far I have not found any that does not precipitate it. No only saline solutions do this, but even a solution of gum arabic.

Neutral salts may precipitate the silver in either a soluble or an insoluble form. Alkaline sulphates, nitrates, and citrates throw down the soluble form; magnesium sulphate, cupric sulphate, ferrous sulphate, nickel sulphate, potassium bichromate and ferrocyanide, barium nitrate, even silver nitrate, and other salts throw down a perfectly insoluble form. The soluble form constitutes a blue or bluish black precipitate; the insoluble, a purple brown, which, by repeated washing, by decantation, or otherwise, continually darkens.

What is very curious is that the insoluble form may be made to return to the soluble condition. Many substances are capable of effecting this change. Sodium borate does so, producing a brown solution, potassium and sodium sulphate produce a yellowish red solution, and ammonium sulphate a red one. None of these solutions has the same blood-red colour as the original solution; the form of silver seems to change with the slightest change of condition.

The solutions used must be extremely dilute, otherwise the silver, though rendered soluble in pure water by them, will not dissolve in the solution itself, a singular complication of effects. So that if a moderately strong solution of one of the above substances is poured over the insoluble silver substance it does not dissolve, but by pouring off the saline solution and replacing it with pure water, the substance now dissolves readily. The insoluble substance is also readily soluble in ammonia. The solution has a fine red colour, and not the yellowish red of the sodium sulphate solution.

Most neutral salts act in one or other of the ways just described, precipitating the solution of the blue substance A in either the soluble or the insoluble form, the latter so uble in ammonia, but sodium nitrite is an exception; its solution effects an entire change and renders the substance wholly insoluble, probably re-converting it to normal silver.

Sometimes the substance will spontaneously pass into a soluble form. A specimen, rendered insoluble by precipitation with ferrous sulphate, after much washing began to run through, not only as a suspension, which often happens, but as a solution, clearing itself after a day or two of insoluble portions, and furnishing a rose-red solution. I have kept this solution in a corked vial for eight months, during which time it has remained unchanged.

The general properties of this substance can be much better observed in the thin films obtained by brushing the moist substance over paper than in the lumps. The films thus obtained are bright greenish metallic, and this green evidently results from a mixture of blue and yellow, as in some lights the blue, in others the yellow, is most evident. When these films are examined by light reflected from them at a large incidence with the normal and a Nicol's prism, or an achromatised prism of calc-spar is interposed between the film and the eye, it becomes at once apparent that the blue and yellow light are oppositely polarised. The yellow light is polarised in the plane of incidence, the blue light perpendicularly to that plane. All specimens show the yellow light, but the quantity of blue light is very variable and is directly connected with the amount of washing applied to the precipitate. The more it is washed the more the yellow predominates. To see the blue form in its full beauty, a little of the red solution may be precipitated with a very little magnesium or aluminium sulphate and be thrown on a filter. As soon as the liquid has drained off and, without any washing, the deep bronze-coloured substance is to be brushed over paper. On drying it has all the appearance of a bright blue metal with a remarkable lustre. The mirrors obtained by brushing the substance over glass are so beautiful and so perfect that it seems as if this property might have useful applications, especially for silvering irregular surfaces. Much care, however, would be necessary in the preparation to obtain a permanent product.

Crystallisation.—On one occasion this substance was obtained in a crystalline form. Some crude red solution had been set aside in a corked vial. Some weeks after, it was noticed that the solution had become decolourised with a crystalline deposit at bottom. The bottle was carefully broken; the deposit, examined by a lens, consisted of short black needles and thin prisms. Evidently the saline matters present had balanced the silver in solution so nearly as not to cause an immediate precipitation, but a very gradual one only. The mother-water was drained off and a few drops of pure water were added. No solution took placed; the crystals were therefore of the material B, the insoluble form. The contact of pure water instantly destroyed the crystallisation, and the substance dried with a bright green metallic lustre. Contact with pure water evidently tends always to bring this form of silver into the colloidal state, sometimes soluble and sometimes not; whilst the contact with certain neutral salts renders it crystalline.

The extraordinary sensitiveness which allotropic silver shows to external influences contrasts strongly with the inertness of normal (probably polymeric) metallic silver. When we place this fact alongside of the well-known sensitiveness of many silver compounds to light, heat, and (as I have elsewhere shown) to mechanical force,* we are led to ask whether silver may not exist in this form in these very sensitive compounds.

To obtain the substance in a pure condition suitable for analysis, it is necessary to choose a precipitant not giving an insoluble product with either citric or sulphuric acid.

* *American Chemical Journal*, Vol. xxxvii., No. 222.

* Production of an image on silver iodide capable of development by simple pressure.

Magnesium sulphate or nickel sulphate answers well; I have generally used the first named. A very dilute solution is made of it, and the red solution of A is to be filtered into it. The precipitate soon subsides. A large quantity of water is to be poured on, and then washing by decantation can be continued to three decantations, after which the substance remains suspended. It can be made to subside by adding a very small quantity of magnesium sulphate; one four-thousandth part (0·25 grm. to one litre) is sufficient. The substance may then be thrown on a filter and washed with pure water.

Analysis.—A specimen dried in vacuo over sulphuric acid gave—

No. 1	.. .. ..	97·17 per cent silver
No. 2	.. .. ..	97·10 ,, ,,

A specimen dried first in vacuo and then at 100° C., lost in the second drying 0·88 per cent water.

So that the substance dried at 100° contained 97·96 per cent of silver. The remaining 2·04 per cent consisted of ferric oxide and citric acid.

C. *Gold-yellow and Copper-coloured Silver.*

It has been long known that golden-yellow specks would occasionally show themselves in silver solutions, but could not be obtained at will, and the quantity thus appearing was infinitesimal. Probably this phenomenon has often led to a supposition that silver might be transmuted into gold.* This yellow product, however, is only an allotropic form of silver, but it has all the colour and brilliancy of gold, a fact which was apparent even in the minute specks hitherto obtained.

By the means presently to be described, silver can be converted wholly into this form. It is a little curious that its permanency seems to depend entirely on details in the mode of formation. I found many ways of obtaining it, but in a few months the specimens preserved changed spontaneously to normal silver. This happened even in well-closed tubes. The normal silver produced in this way is exquisitely beautiful. It has a pure and perfect white colour like the finest frosted jewellers' silver, almost, in fact, exceeding the jewellers' best products. I found, however, one process by which a quite permanent result could be obtained. Specimens made by it in November of 1886 are now, at the end of thirty months, unchanged.

In forming the blue product which I have called A, very concentrated solutions were necessary. C, on the contrary, is best obtained from very dilute ones. The following proportions give good results:—

Two mixtures are to be prepared: No 1 containing 200 c.c. of a ten per cent solution of silver nitrate, 200 c.c. of twenty per cent solution of Rochelle salt, and 800 c.c. of distilled water. No 2 containing 107 c.c. of a thirty per cent solution of ferrous sulphate, 200 of a twenty per cent solution of Rochelle salt, and 800 of distilled water. The second solution (which must be mixed immediately before using only) is poured into the first with constant stirring. A powder, at first glittering red, then changing to black, falls, which on the filter has a beautiful bronze appearance. After washing it should be removed whilst in a pasty condition, and spread over watch-glasses or flat basins, and allowed to dry spontaneously. It will be seen that this is a reduction of silver tartrate by ferrous tartrate. The metallic silver formed by reduction with ferrous citrate and ferrous tartrate is in an allotropic condition; with ferrous oxalate this result does not seem to be produced.

Although the gold-coloured silver (into which the nitrate used is wholly converted) is very permanent when dry, it is less so when wet. In washing, the filter must be kept always full of water: this is essential. It dries into lumps exactly resembling highly polished gold, especially the surfaces that have dried in contact with glass or porcelain. For this substance has in a high degree the property already described in forms A and B—that of drying with the particles in optical contact. When the thick pasty substance is extended over glazed paper, it dries with the splendid lustre of gold leaf, with this essential difference—that these allotropic forms of silver B and C assume spontaneously in drying the high degree of brilliancy which other metallic surfaces acquire by elaborate polishing and burnishing. By brushing a thick paste of this substance evenly over clean glass, beautiful gold-coloured mirrors are obtained; the film seems to be entirely continuous and the mirror is very perfect.

By continued washing the precipitate changes somewhat, so that in drying it takes on a coppery rather than a golden colour, and is rather less lustrous, though still bright and permanent.

Two silver determinations by conversion into chloride made in Nov., 1886, gave—

No. 1	.. .. ..	97·81 per cent silver
No. 2	.. .. ..	97·86 ,, ,,

Recently these experiments have been repeated, and the washing was more successful. Ferric tartrate adheres very obstinately, and after a time washing with water ceases to remove it. Stronger means cannot be employed without affecting the substance itself. These last determinations gave—

No. 1	.. .. ..	98·750 per cent of silver
No. 2	.. .. ..	98·749 ,, ,,

The residue of No. 2 was examined and consisted almost wholly of ferric citrate.

Note.—(By the Editors of the *American Journal of Science*).—The editors have received, from the author of the above paper, samples of the three allotropic forms of silver which he describes, and also strips of glass and paper coated with them. Mr. Lea is to be congratulated on his very important results. The coated strips, including the gold-coloured mirror made with the "gold-silver," answer fully to his description. The mirror is remarkable for its perfection and brilliancy.

THE AMMONIO-COBALTIC MOLYBDATES, TUNGSTATES, AND VANADIATES. SEPARATION OF COBALT AND NICKEL AND OF THE COBALTOUS AND COBALTIC SALTS.

By ADOLPHE CARNOT.

It is known that the ammonio-cobaltic salts differ in several of their characters from the corresponding salts of cobaltous oxide and of nickel. But these characters are not, in general, sufficiently distinct to serve for the recognition and the separation of these salts. This advantage the author finds in certain new salts, the molybdates, tungstates, and vanadiates. For the present he speaks of the molybdates only. If a solution of cobalt is converted into a purpureo-cobaltic salt by oxygenated water in presence of ammonium chloride and ammonia, as formerly indicated (*Comptes Rendus*, April 8th. 1889), and if ammonium molybdate is added, there ensues no turbidity and no change of colour. But if the liquid is neutralised and acidified with acetic acid there is at once produced a bulky precipitate of a fine peach-blossom

* I have a little volume published in Paris in 1857 by a chemist named Tiffereau who was firmly convinced that in many reactions minute portions of silver are converted into gold, especially with the aid of powerful sunlight. In Mexico, he affirmed, he had artificially produced several grms. of gold, a portion of which he presented to the French Academy with one of his papers. To his great disappointment he did not succeed in repeating these experiments in Paris with more than an infinitesimal result. All gold in his opinion had been originally silver, and this belief, he affirms, is universal among Mexican miners. The book has for title "Les Métaux sont des Corps composés."

colour. This precipitate, which is almost absolutely insoluble, collected on a filter, washed, and dried at 100°, remains of a rose colour. If heated more strongly it takes a violet tint and passes through blackish green and greenish yellow colours, changes which correspond to successive eliminations of water, of ammonia, and of oxygen. The matter becomes a cobaltous molybdate and has a lilac colour when cold. If the temperature of dull redness is exceeded it undergoes a partial dissociation with formation of black cobalt oxide and of molybdic anhydride in small crystals.

The analysis of the rose-coloured salt, dried at 100°, was excecuted by decomposing with potassa-lye, collecting the ammonia in a standard solution of sulphuric acid, isolating the insoluble cobalt peroxide, and determining the cobalt after reduction by hydrogen. Lastly, the alkaline molybdate was converted into sulphomolybdate and the molybdenum weighed as sulphide. The water was calculated as difference. The author gives the composition of the dried salt as $Co_2O_3,5NH_3,7MoO_3 + 3HO$, and when calcined, $2CoO.7MoO_3$.

The salts of cobaltous oxide and the nickel salts give no precipitate with ammonium molybdate either in an acetic or an ammoniacal precipitate. A crystalline deposit of the double ammonium and cobalt (or nickel) may indeed be formed, but it is only produced slowly and in liquids which are nearly neutral and very concentrated, conditions easily avoided.

The reaction just indicated gives the means, not previously possessed, to recognise the ammonio-cobaltic salts, and even to determine them in presence of cobaltous salts. It is merely necessary to acidify the solution with acetic acid and to add the molybdic reagent. The precipitate will contain all the ammonio-cobaltic salt and the liquid all the cobaltous salt. We may in this manner solve various questions, and even follow the progress of the peroxidation of cobalt in ammoniacal solutions left to themselves or traversed by a current of air. The same method enables us to separate cobalt and nickel, as the latter is not peroxidised by hydrogen peroxide in an ammoniacal solution. The following are the necessary details of the operation:—

The two metals being in a hydrochloric or nitric solution we add ammonium chloride and ammonia in excess and then a little oxygenated water. After a few minutes the mixture is gently heated to a boil. When the effervescence due to the escape of oxygen has completely ceased it is let cool. Cold water is added if the colour of the liquid shows that it is too concentrated. We neutralise with acetic acid and add further 3 to 5 c.c. of this acid to 100 c.c. of the liquid and then add a solution of ammonium molybdate until no further turbidity is occasioned. It is let settle, decanted, and the precipitate is received upon a filter and washed with water and a few drops of ammonium chloride. After desiccation it can be easily and almost completely separated from the paper, which is burnt separately. Lastly, the precipitate is ignited, but without exceeding dull redness. It is then let cool and weighed. The weight is multiplied by the coefficient 0·1332 to find the weight of the cobaltous oxide and by 0·1048 to have that of the metal. The weight of the ignited molybdate is therefore approximately ten times that of the cobalt.

The rose-coloured precipitate of ammonio-cobalt molybdate is very bulky and very characteristic. The method furnishes consequently a highly sensitive method of qualitative detection, showing traces of cobalt in the commercial salts of nickel. It is applicable also in presence of copper and zinc.

The separation of the metals, as well as the determination of the cobalt, is very exact, especially for small quantities, from some milligrms. up to at most 1 decigrm. The better to remove foreign salts, it is well to re-dissolve the precipitate while still moist in ammonia-water, and to re-precipitate by rendering the liquid slightly acetic and adding a little ammonium molybdate.

To determine the nickel in the filtrate a sufficient quantity of caustic potassa is added, and the liquid is heated to ebullition, so as to expel the ammonia and entirely precipitate the nickel hydroxide. It is received on a filter, re-dissolved in hydrochloric or nitric acid, and precipitated afresh, using potassa and bromine. The sesquioxide obtained retains not a trace of molybdate, and may be determined either by means of a standard solution or by reducing in hydrogen and weighing the metallic nickel.—*Comptes Rendus* (vol. cix., p. 109).

A CONVENIENT FORM OF PIPETTE FOR MEASURING OUT BEET, CANE, AND SORGHUM JUICES FOR POLARISATION.

By C. A. CRAMPTON.

In "Bull. No. 15, Chem. Div. U.S. Dept. Agr.,"* I have described the method of procedure followed by the analysts at the Stations of this Department in the analysis of juices. For polarisation it has been the custom to measure out a sample of juice, as it would require too much time to weigh, and for this purpose it has been the custom to measure out 50 c.c. with a pipette,

making subsequent correction of the polarisation for the specific gravity of the juice. When the polariscope used is one that has the factor 26·048, that is, requires 26·048 grms. of pure sugar, dissolved and made up to 100 c.c. of water, to read 100 on the scale, it will be seen that 50 c.c. of juice gives a weight in grms. very nearly twice the normal amount to be taken for the instrument, or 52·096. Last year I had some pipettes made, which were graduated in the stem from 48 to 54 c.c., with sub-divisions of 0·5 c.c., to be used in measuring out directly the correct amount of juices of different densities, to give double their polarisation; the number of c.c. to be used for each

* Also in Chem. News, lv., 207.

density to be ascertained from a table. These pipettes were used during the present sugar campaign in Louisiana by Mr. G. L. Spencer, at Magnolia Station, who found them very convenient. He has calculated a table to be used in connection with them.

I have had made recently a modification of this pipette, which does away with the necessity of a table, and which is illustrated in the accompanying cut. It is graduated from 48·1 to 51·1 c.c., the sub-divisions being in tenths of a c.c., but the divisions are marked instead with degrees Brix, having a range from 5° to 20° each, 0·1 c.c. division corresponding to 0·5° Brix. That is, after the degree Brix of a juice has been ascertained, the pipette, when filled up to the corresponding mark on the stem, will deliver 52·096 grms. of the juice (within a few m.grms., which is as close as it is possible to weigh it out). So it is necessary to divide the polarisation by two, or to read the solution in a 400 m.m. tube, to give directly the per cent of sucrose in the juice.

The calculation for the graduations is taken from Stammer's table for specific gravities and the corresponding degrees Brix. For commercial work these pipettes will weigh out the juice with sufficient accuracy, and I think they will prove convenient for rapid work, and save considerable time in the calculation of results.—*Journal of Analytical Chemistry*, Vol. iii., Part 1.

ANALYSES OF SOME CISTERN-DEPOSITS.

By ALFRED S. CHAPMAN, F.C.S.

A short time ago Professor Graham, of University College, handed me three mineral deposits, taken from a copper cistern in which water had been softened by Clark's process, and suggested that I should submit them to analysis. The results are, I venture to think, of sufficient interest to warrant their publication. These three substances I shall refer to, for sake of simplicity, as A, B, and C.

Deposit A.—This was a very hard grey stone; a broken surface having a slightly rough and crystalline appearance. Its weight was about 6 grms.

Deposit B.—A hard stone of a light buff colour. It was of a very compact nature, a broken surface appearing perfectly smooth. It weighed about 4·5 grms.

Deposit C.—A rough green-coloured deposit, somewhat resembling terre-verte in appearance. It was very much softer than either A or B, and weighed only 0·6 grm.

The following are the results of the analysis of deposit A:—

Lime	52·19
Oxide of iron	8·40
Silica	19·68
Carbonic acid	5·70
Water of combination ..	13·60
Trace $MgSO_4$ &c.	0·43
	100·00

After converting the carbonic acid into its equivalent of carbonate of lime (= 12·95 per cent) and then combining the silica with as much lime as is required to form the neutral silicate, it will be found that there is still 26·58 per cent lime left uncombined, which I have every reason to believe exists in combination with the calcic silicate and water, forming a hydrated basic silicate. After converting the 5·7 per cent carbonic acid into 12·95 per cent carbonate of lime there is 44·94 per cent lime left. The ratio of this number (the amount of lime existing as a basic silicate) to the percentage of silica (19·68) is as 2·20 : 1.

I shall refer to this ratio in connection with the next analysis:—

Results of Analysis of Deposit B.

Lime	53·20
Oxide of iron	1·80
Magnesia	0·32
Carbonic acid	34·37
Silica	4·30
Sulphuric acid	0·71
Water of combination, moisture, &c., by difference	5·30
	100·00

In this case, after combining the lime with the silica (to form the neutral silicate) and with the carbonic acid, there is 5·45 per cent uncombined lime. If, as in the last case, the 34·37 per cent carbonic acid be converted into 78·11 per cent carbonate of lime there remains 9·46 per cent lime. The ratio of this number, which is the amount of lime existing probably as a hydrated basic silicate, to the percentage of silica (4·30) is as 2·28 : 1. Hence it appears permissible to conclude that in each of these two deposits there exists a basic silicate of lime of the same composition. The mean of these two ratios (2·24 : 1) is very nearly that which would occur in the compound $2CaSiO_3.3CaO$.

There was not sufficient of B for a direct determination of the water of combination, but if, in the analysis of A, the ferric oxide be converted into ferric hydrate, the remaining water and the percentage of lime and silica are nearly those numbers which would be required for the compound $2CaSiO_3.3CaO+4H_2O$.

Examination of Deposit C.

This substance, which I thought at first might be a basic carbonate of copper, I found on examination to contain, in addition to copper and carbonic acid, considerable quantities of silica and arsenic. The quantity at my disposal (0·6 grm.) was too small for a complete quantitative analysis, but the following are some results obtained:—

Silica	19·8 per cent.
Carbonic acid .	1·8 ,,

A determination of the arsenic gave rather more than 5 per cent, but this number is only approximate.

University College, July 18, 1889.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, June 20th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

(Concluded from p. 49).

67. "*Note on the Oxidation of Paradiamines.*" By R. Meldola, F.R.S., and R. E. Evans.

It is well known that quinones are formed by the oxidation of benzenoid paradiamines, and it is generally believed that the amido-groups are split off in the form of ammonia, but it does not appear that any quantitative determination of the amount of ammonia produced has been made. The authors have, therefore, made a series of experiments with paraphenylenediamine prepared by the reduction of paranitraniline, using the base in the form of the sulphate, this salt being easily purified by crystallisation. After several preliminary trials, the most convenient mode of procedure was found to be as follows:—The calculated quantity of potassium dichromate was dissolved in water, and the solution of the diamine sulphate poured in; the mixture was allowed to stand for two days at the ordinary

temperature, and then filtered to remove the quinone and its associated impurities. The filtrate was made distinctly acid with dilute sulphuric acid, and evaporated on a water-bath to a small bulk, then transferred to a flask and made alkaline with caustic soda. The ammonia was driven off by a current of steam, and received in dilute chlorhydric acid. The distillate was evaporated to dryness in a weighed dish, and the dry residue weighed as ammonium chloride. 5 grms. of paraphenylenediamine sulphate treated in this way gave 2·38 grms. of ammonium chloride. The quantity required by theory is 2·6. The ammonium chloride was tested qualitatively, and found to be free from impurities.

68. "*Monobenzyl-derivatives of the Phenylenediamines.*" By R. Meldola, F.R.S., and J. H. Coste.

Monobenzylparaphenylenediamine was prepared by reducing monobenzylparanitraniline (Meldola and Salmon, *Trans.*, 1888, 774) with tin and chlorhydric acid, and removing the tin as sulphide. The dihydrochloride, $C_6H_4 \cdot NH_2 \cdot NH \cdot C_7H_7 \cdot 2HCl$, forms lustrous white scales readily soluble in water, less soluble in chlorhydric acid, and almost insoluble in alcohol. Ferric chloride gives a green colouration when added to the aqueous solution, this colour soon changing into red. The diacetyl-derivative, $C_6H_4 \cdot NHAc \cdot NAc \cdot C_7H_7$, forms colourless hexagonal prisms melting at 116·5—117°. The dibenzoyl-derivative forms white needles melting at 124°. One mol. prop. of the benzyldiamine oxidised in the presence of one of benzylaniline gives the dibenzylindamine, $C_7H_7 \cdot HN \cdot C_6H_4 \cdot N:C_6H_4:N \cdot C_7H_7$. This compound, which is of an intense greenish blue colour with a coppery lustre, rapidly undergoes spontaneous decomposition, and becomes converted into what is apparently a mixture of benzylbenzylidene- and dibenzylidene-diamidodiphenylamine,—

$$NH\!<\!\begin{matrix} C_6H_4 \cdot N:CH:C_6H_5 \\ C_6H_4 \cdot NH \cdot CH_2C_6H_5 \end{matrix} \text{ and } NH\!<\!\begin{matrix} C_6H_4 \cdot N:CH \cdot C_6H_5 \\ C_6H_4 \cdot N:CH \cdot C_6H_5 \end{matrix}.$$

One molecule of the benzyldiamine oxidised in the presence of two molecules of benzylaniline at the temperature of boiling water gives an azine or benzylated saffranine, which is of interest as being produced, in contradiction to the generally received view, from one molecule of a diamine and two molecules of a *secondary* monamine. The free amido-group of the benzyldiamine can be diazotised by the action of nitrous acid, and the diazo-salts combine with phenols in the usual way to produce azo-compounds. Of the latter, the azo-derivatives of α- and β-naphthol have been prepared. The free base, benzylparaphenylenediamine, has been isolated, and forms reddish moss-like crystalline aggregations; the melting-point is 30°; the base reddens by oxidation on exposure to the air. Monobenzylmetaphenylenediamine was prepared in a similar manner to the above by reducing benzylmetanitraniline. The free base is oily at the ordinary temperature; the dihydrochloride forms dense laminated rhombohedra of an ochreous colour. The aqueous solution of the latter salt gives a red colour passing into orange-brown on the addition of ferric chloride. On heating the solution with ferric chloride or other oxidising agent a white insoluble product of oxidation settles out. The diacetyl-derivative of the benzylmetadiamine forms an uncrystallisable resin; the dibenzoyl-derivative forms rhomboidal plates melting at 178°. By oxidising equi-molecular proportions of the benzylmeta- and benzylpara-diamines, a deep indigo-blue indamine i precipitated. This colouring matter is fairly stable in th cold, but passes into an azine on heating.

69. "*Note on a Yellow Pigment in Butterflies.* By F. Gowland Hopkins.

For the most part the colour effects on the wings of lepidopterous insects are probably due to purely physical causes, and not to the presence of any definite pigment. But in some cases pigments are undoubtedly present. These are for the most part very difficult to isolate; but an exception to the rule occurs in the case of a certain yellow pigment which is found in its purest form in the common English brimstone butterfly. The pigment may also be detected in the wings of a very large number of day-flying lepidoptera. It may be obtained from the wings by simple treatment with hot water, in which it is freely soluble, and it may be identified by its yielding a marked murexide reaction when evaporated with nitric acid and afterwards treated with ammonia or potash.

The wings should be first treated with hot alcohol and ether, in which the pigment is insoluble, then boiled up with water, and the yellow aqueous solution filtered while hot. If the aqueous solution be now concentrated to a small bulk and allowed to cool, the substance separates out as a yellow amorphous precipitate. It may be purified by dissolution in a fresh quantity of hot water, whence it again separates on cooling. Otherwise it may be removed from the wing by the action of dilute alkalies in the cold, and afterwards precipitated by the addition of acetic acid. The common brimstone butterfly yields somewhat less than a m.grm. of pigment from each insect; larger foreign species, such as those belonging to the genus *Callidryas*, may yield as much as 4—5 m.grms.

The pigment is an amorphous powder insoluble in alcohol, ether, chloroform, and all the more common organic solvents. It is very sparingly soluble in cold, but freely so in hot water.

Its aqueous solutions have a fine blue fluorescence and are strongly acid to litmus. The substance is freely soluble in alkalies, yielding with them solutions darker in colour than is its aqueous solutions; from these it is precipitated when neutralised with acetic acid.

It thus agrees closely in its physical properties with *mycomelic acid*, a yellow derivative of uric acid, though its yellow colour is more decided than is that of the latter substance. Mycomelic acid does not, however, yield a murexide reaction; while the pigment, as stated above, does so in a very marked manner. If it be boiled for some time with chlorhydric acid it is decomposed, and crystals of uric acid separate out, coloured much in the same manner as when obtained from acidified urine; on prolonged boiling with the dilute acid, urea is formed together with other crystalline substances not yet determined. There can be no doubt that the pigment is a derivative of uric acid, probably allied to mycomelic acid. It appears not improbable to the author that it may indeed be a condensation product of the two acids uric and mycomelic, and progress towards its synthesis has been made in this direction. If it be supposed that the two acids unite with elimination of two mols. of water to form a new dibasic acid, the acid would yield a silver compound containing 44·44 per cent of silver. The pigment under discussion gives a perfectly definite silver compound, the amount of silver found in three analyses being 44·61, 44·66, and 44·42 per cent.

The author hopes shortly to obtain a sufficiency of the substance for accurate ultimate analysis.

70. "*Zinc Dextrosate.*" By A. C. Chapman.

This compound is prepared by dissolving zinc hydrate in the smallest possible quantity of ammonia solution, and adding the liquid to a solution of dextrose in 90 per cent alcohol; its composition is represented by the formula $C_6H_{12}O_6 \cdot 2ZnO \cdot 3H_2O$.

71. "*β-Bromonaphthalenesulphonic Acid.*" By R. W. Sindall.

Whereas the two isomeric acids obtained on sulphonating β-chloronaphthalene by means of SO_3HCl —no heat being applied except in distilling off the carbon disulphide used as solvent of the chloronaphthalene—have been shown to correspond respectively to the so-called Badische and Brönner modifications of beta-naphthylaminesulphonic acid, the 2 : 1′ being the chief, and the 2 : 3′ the subsidiary product, the experiments made by Mr. W. Houlding (*Chem. Soc. Proc.*, 1889, 74) have shown that in the case of β-iodonaphthalene the result is different, inasmuch as the β-iodo-acid prepared

from the Brönner β-amido-acid is not identical with either of the two β-iodo acids formed by direct sulphonation of β-iodonaphthalene. Mr. Houlding has shown that the bromo acid prepared from the Brönner β-amido acid is identical with the minor product of sulphonation of β-bromonaphthalene; to determine the nature of the major product of sulphonation, the author has prepared the isomeric acids from the three isomerides of Brönner's β-amido acid.

2 : 1′ *Bromonaphthalene-α-sulphonic Acid.*— Although this acid has been prepared by Forsling (*Ber.*, 1889, 619), the account which he gives is insufficient for the purposes of comparison. The author finds, as was to be expected, that the bromo-acid prepared by the Griess-Sandmeyer process from the Badische β-amido-acid is identical with the major product of sulphonation of β-bromonaphthalene (cf. *Chem. Soc. Proc.*, 1887, 23). The sulphochloride melts at 147°; the sulphobromide, as stated by Forsling, at 151°; the sulphonamide melts at about 209°.

2 : 4′ *β-Bromonaphthalene-α-sulphonic Acid.*—This acid was prepared from the Dahl β-amido-acid. Its sulphochloride crystallises well from light petroleum in aggregates of small prisms melting at 77°; the sulphonamide melts at about 217°.

2 : 2′ *β-Bromonaphthalene-β-sulphonic Acid.* — Mr. Houlding had prepared this acid from the δ- (Bayer and Duisberg) amido-acid; the author has repeated the experiments. The sulphochloride crystallises from benzene in massive, oblique prisms melting at 100°; the sulphonamide melts at about 218°.

On distilling the sulphochlorides of the four β-bromo-acids with phosphorus pentachloride, the product obtained chiefly consists of the corresponding *dichloronaphthalene*, both the bromine atom and the SO_2Cl group becoming displaced by chlorine. In Mr. Houlding's paper (*loc. cit.*) the melting point 137° is wrongly assigned to 2 : 3′ chlorobromonaphthalene.

72. "*Isomeric Change in the Naphthalene Series.* No. 5. *β-Iodonaphthalenesulphonic Acids.*" By Henry E. Armstrong and W. P. Wynne.

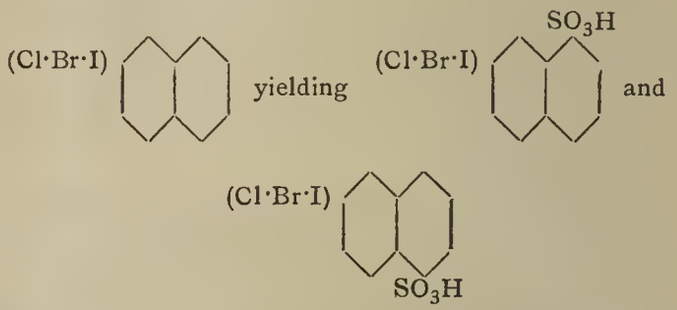
The authors describe the results obtained on carrying out the experiments referred to at the close of a recent communication by Mr. W. Houlding (*Chem. Soc. Proc.*, 1889, 74, *cf. infra*).

2 : 2′ *β-Iodonaphthalene-β-sulphonic Acid.*— This acid was prepared by Mr. Houlding from betanaphthylamine-δ-sulphonic acid. Its sulphochloride crystallises from benzene in aggregates of small prisms melting at 100°; its sulphonamide melts at 210°. It is not identical with either of the acids produced on sulphonating β-iodonaphthalene.

2 : 1′ *β-Iodonaphthalene-α-sulphonic Acid.*—The authors have prepared this acid from the Badische modification of betanaphthylaminesulphonic acid, and find that, as was to be supposed, it is identical with the major product of sulphonation of β-iodonaphthalene by SO_3HCl. It is to be noted, however, that the sulphochloride melts at 164—165°, and not at 174° as by mistake has been previously stated (*B.A. Report*, 1887, 234), the sulphonamide melts at about 240°.

2 : 4′ *β-Iodonaphthalene-α-sulphonic Acid.* — On preparing this acid from the Dahl modification of betanaphthylaminesulphonic acid, it was found to be identical with the acid obtained as minor product on sulphonating β-iodonaphthalene by means of SO_3HCl. The sulphonchloride melts at 92·5°; the sulphonamide at about 213°.

Although, therefore, the major product of sulphonation in the case of β-chloro-, bromo-, and iodonaphthalene is the 2 : 1′ *alpha*-sulphonic acid, the minor product is different: β-iodonaphthalene yielding a second *alpha*-sulphonic acid, whereas β-chloro- and bromo-naphthalene each give the 2 : 3′ *beta*-sulphonic acid; and it should also be stated that a smaller proportion of the acid which is the subsidiary product is obtained both from chloro- and from bromo- than from iodonaphthalene. Two explanations of the dissimilarity are possible, viz.: either that there is an initial difference of behaviour or that there is no initial difference, but that isomeric change takes place in the case of the chloro- and bromo-. and not in the case of the iodo-compound. The latter appears the more probable. It may be supposed that initially on sulphonation two isomeric acids are formed—



and that in the case of chloro- and bromo-naphthalene one of these — the 2 : 4′ acid — *at once spontaneously* undergoes isomeric change into the 2 : 3′ isomeride, no such alteration, however, occurring in the case of the iodo-acid. There is much independent evidence that such a change may well occur: thus on sulphonating 1 : 4 dichloronaphthalene a heteronucleal dichloro*beta*-sulphonic acid is obtained as sole product; but there is every reason to believe that the actual product of sulphonation is an *alpha*-acid, and if this be the case isomeric change must take place spontaneously, and with exceptional facility and completeness. 1 : 3 Dichloronaphthalene yields only an alpha-sulphonic acid. 1 : 2 Dichloronaphthalene, however, affords a mixture of about two-thirds 1 : 2 : 4′ *alpha*-sulphonic acid with one-third of the isomeric 1 : 2 : 3′ *beta*-sulphonic acid (cf. *Chem. Soc. Proc.*, 1889, 52); this latter the authors believe to be a product of spontaneous isomeric change occurring at the moment of sulphonation, and that this is the case is placed almost beyond question by the observation that if the mixed product of sulphonation be heated at 150—160° during ten hours, the alpha-sulphonic acid almost entirely disappears, the beta-acid taking its place.

It has previously been shown that 2 : 1′ β-chloronaphthalene-α-sulphonic acid is converted into the 2 : 3′ acid by heating it at about 150° (cf. *Chem. Soc. Proc.*, 1887, 145). The 2 : 1′ iodo-acid should therefore be convertible into the 2 : 3′ isomeride, and this is found actually to be the case. The product obtained on sulphonating β-iodonaphthalene and then heating the resulting mixture of alpha-acids at 150° during about five hours, in fact, consists almost entirely of the 2 : 3′ iodo-acid identical with that prepared from the Brönner betanaphthylaminesulphonic acid, showing clearly that not only the 2 : 1′ but also the 2 : 4′ acid passes by isomeric change into the symmetric ββ 2 : 3′ acid.

73. "*The Formation of Sulphones on Sulphonating Naphthalene Derivatives by means of Chlorosulphonic Acid.*" By W. M. Heller.

When naphthalene and its monohaloid derivatives are sulphonated by means of SO_3HCl, a varying but always small proportion of sulphochloride is usually obtained, but apparently this is a secondary product, and results from the action of the SO_3HCl on the sulphonic acid which is first formed.

On sulphonating 1 : 4 chlorobromonaphthalene, dissolved in carbon bisulphide, by SO_3HCl, using equimolecular proportions of the interagents, the author has found that the whole of the naphthalene compound is acted on, but that only a relatively small amount of sulphonic acid is obtained, the chief product being the sulphone,—

$$(C_{10}H_5ClBr)_2SO_2,$$

no sulphochloride being formed. The corresponding β-dichloro- and dibromo-naphthalene behave similarly. The melting points of the sulphones thus obtained, and

of the sulphochlorides prepared from the corresponding sulphonic acids, are as follows :—

$\beta Cl_2 \cdot SO_2Cl$	133°	Cl_2 sulphone about	216°
$\beta ClBr \cdot SO_2Cl$	—	ClBr ,,	224°
$\beta Br_2 \cdot SO_2Cl$	119°	Br_2 ,,	236°

The sulphones are almost insoluble in benzene, but may be crystallised from xylene.

On sulphonating γ-dichloronaphthalene (m. p. 107°) by SO_3HCl, a small amount of a compound melting at 265° is obtained, which probably is also a sulphone. The corresponding chlorobromonaphthalene, however, appears to yield only sulpho-acid ; the chloride of this acid melts at about 155°.

74. "*Note on the Hydration of Cyanides.*" By Henry E. Armstrong.

Experiments made at the author's request by Mr. Houlding with the object of comparing the behaviour towards sulphonating agents of β-cyanonaphthalene with that of α-cyanonaphthalene have shown that, unlike the latter, the β-compound is not susceptible of sulphonation ; if, however, it be dissolved in fuming sulphuric acid and the solution be cautiously poured into water, it is completely converted into β-naphthoeamide, $C_{10}H_7 \cdot CO \cdot NH_2$.

In like manner, Mr. Percival has found that on adding trichloracetonitril, $CCl_3 \cdot CN$, to sulphuric anhydride a liquid is obtained which gradually solidifies to a mass of crystals of a compound of the nitril with the anhydride; on adding this compound to water, it undergoes immediate and complete conversion into trichloracetamide.

These two cases appear to afford striking evidence in favour of the view that hydrating and hydrolytic agents act by forming compounds directly attackable by water ; they serve, in fact, to support the integration rather than the dissociation hypothesis of chemical change. It is not improbable that the non-conversion of pentamethylbenzonitril into the corresponding acid to which Hofmann has called attention, and the recent similar observation made in Victor Meyer's laboratory (*Annalen*, 250, 147) are to be explained as consequences of the incapability of the cyanide in question to form compounds with the hydrating agents used; and that perhaps sulphuric anhydride will be found available in these cases also.

75. "*The Existence of Salicylic Acid in Certain Genera of the Lilaceæ.*" By A. B. Griffiths.

The author states that he has isolated salicylic acid from the leaves, stems, &c., of *Tulipa*, *Yucca*, and *Hyacinthus* in the following manner :—

The leaves, stems, &c., cut up into small pieces, were digested with ether and the solution distilled. The residue was treated with distilled water and the solution filtered ; the filtrate was then neutralised with potassium carbonate, evaporated, and finally distilled with pure chlorhydric acid. The aqueous distillate yielded on evaporation colourless, prismatic crystals, which were found to be soluble in ether, alcohol, and boiling water, but sparingly soluble in cold water.

A solution of the crystals gave with ferric chloride a deep violet colour. A series of combustion analyses of these crystals were carefully performed, which he states gave the composition of salicylic acid. The crystals were found to melt at 131° C., and on distilling them with lime, phenol and carbon dioxide were readily produced.

The author states that he has estimated the percentage of the acid in various parts of the plants with the following results :—

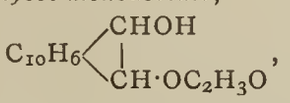
	Tulipa.	Yucca.	Hyacinthus.
Leaves	0·0989	0·1410	0·1103
Peduncles ..	0·0812	—	0·0788
Stems	—	0·1065	—
Bulbs	0·0542	—	0·0483
Flowers ..	trace	—	trace

76. "*On the Oxidation Products of Acenaphthene.*" By T. Ewan, B.Sc., and J. B. Cohen, Ph.D., Owens College.

These experiments were undertaken with the view of preparing the products of oxidation intermediate between acenaphthene and naphthalic acid.

By the action of lead oxide and water upon dibromacenaphthene bromide, a yellow crystalline compound melting at 126—129° was obtained, which has the formula $C_{12}H_4O_2Br_2$.

Acenaphthylene glycol monoacetate,—



is obtained by converting acenaphthylene dibromide into the acetate, and decomposing the product with potash ; m.p. 122—122·5°.

Acenaphthylene glycol diacetate,—

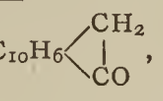
$$C_{10}H_6(CH \cdot OC_2H_3O)_2,$$

is obtained by boiling the monacetate with excess of acetic anhydride ; m.p. 130°.

Acenaphthylene glycol is prepared by decomposing the monoacetate with boiling alcoholic potash. It crystallises in colourless needles melting at 204—205°.

Acenaphthylene glycol monobenzoate is obtained by acting upon the dibromide with silver benzoate. It crystallises in plates melting at 189—190°.

Acenaphthene ketone,—



is prepared from the glycol by the action of sodium alcoholate. It crystallises in pale yellow needles melting at 119—119·5°.

The alkyl ethers of the glycol cannot be obtained by any of the usual reactions. If acenaphthylene bromide be acted on by sodium ethylate in alcoholic solution acenaphthene is formed, and if the bromide be treated with anhydrous sodium ethylate in benzene solution acenaphthylene is produced.

Tetrabromacenaphthene, $C_{12}H_6Br_4$, is formed by the action of bromine dissolved in carbon bisulphide upon acenaphthylene bromide ; m. p. 161—162°.

Tribromacenaphthene, $C_{12}H_7Br_3$, is prepared in a similar manner ; m. p. 88—90°.

Chromium oxychloride reacts with acenaphthene in CS_2 solution, and forms a well-defined addition compound, but the diketone could not be obtained. The authors have prepared crystalline compounds by distilling the barium salt of naphthalic acid with the lime salt of the fatty acids, which are probably the aldehyd and ketone-derivatives of naphthalic acid. Acenaphthene reacts with the acid chlorides in presence of aluminium chloride, forming ketones.

A crystalline compound has also been obtained by the action of PCl_5 upon naphthalimide. The investigation of these compounds will form the subject of a subsequent communication.

77. "*Schutzenberger's Process for the Estimation of the Oxygen Dissolved in Water.*" By Sir Henry E. Roscoe, F.R.S., D.C.L., LL.D., and Joseph Lunt, B.Sc., Associate of the Owens College.

The authors find that a series of estimations made on the same sample of London tap water give results which differ 35 per cent from the mean value, and that the time taken in titrating has a great influence, much higher results being obtained if titration be quickly than if it be slowly performed. The disturbing influence has been traced to the fact that when aërated water is introduced into an atmosphere of hydrogen, as in the usual process, it immediately begins to lose oxygen by diffusion, a fact hitherto overlooked. The result of an oxygen estimation thus depends on the degree of exposure to hydrogen during titration, and results between 0·53 and 7·56 were obtained with the same water by varying the exposure.

Under favourable circumstances 20 per cent of the dissolved oxygen diffuses, whilst in the usual form

of the apparatus 50 per cent of the oxygen diffuses during the estimation. An exposure of three minutes is sufficient to permit all the dissolved oxygen to escape. This explains the return of the blue colour during an estimation carried out in the usual manner, the *diffused* oxygen becoming re-absorbed by the reduced indigocarmine. No return of the blue colour takes place on reducing indigocarmine when free oxygen is absent, and the action has been proved to be due to the supernatant gas, and not to any action occurring within the liquid, as Schützenberger supposed.

Diffusion also explains the observation made by Schützenberger that twice the amount of oxygen is found when a large amount of reduced indigocarmine is present; in that case the dissolved oxygen is at once acted on, and so cannot diffuse.

Ramsay and Williams, who have investigated the process, do not obtain twice the amount, but only an increase in the ratio of 3 : 5. Diffusion also explains this observation, a smaller vessel having been used in their experiments a larger proportion of the oxygen was found in the usual process, in other words, three-fifths of the whole.

The method adopted to eliminate this error, due to diffusion, is to run the aërated water beneath the surface of a liquid containing a measured excess of hyposulphite, and a little reduced indigocarmine as an indicator. In this way the dissolved oxygen is immediately acted on by the hyposulphite and its diffusion prevented. For the standardisation of the hyposulphite the two methods hitherto used were found inaccurate. The copper method being fundamentally wrong owing to a secondary action which occurs between sulphite and dissolved oxygen. The aërated distilled water method, hitherto used with Bunsen's absorption coefficients, the authors show to be inaccurate, giving the values obtained by them, which agree closely with observations made by Dittmar.

The new method of carrying out the process and the corrected values for the oxygen dissolved by distilled water give results for which perfect accuracy cannot be guaranteed, but which are not far removed from the truth, and certainly valuable. The reaction is much disturbed by the presence of free acid or alkali.

78. "*Isomeric Change in the Phenol Series*" (Third Notice). By Arthur R. Ling.

The author finds that chlorine under a variety of conditions does not affect the conversion of ortho- into para-nitrophenol-derivatives; bromine alone appears to have this property.

He corrects a previous statement that orthochloroparabromorthophenol is converted by the action of bromine into parachlororthobromorthonitrophenol.

On treatment with nitric acid parachlororthobromorthonitrophenol yields parachlorodiorthonitrophenol, whereas parabromorthochlorothonitrophenol is converted into orthochloroparadinitrophenol—the bromine and not the chlorine atom being always displaced.

Orthochloroparabrom*orthonitro*phenol appears to undergo isomeric change when treated with bromine, yielding the isomeric orthochlororthobrom*paranitro*phenol together with orthochlordinitrophenol and chlorotribromoquinone.

NOTICES OF BOOKS.

Alkali, &c., Works Regulation Act, 1881. *Twenty-fifth Annual Report on Alkali, &c., Works by the Chief Inspector. Proceedings during the Year* 1888. Presented to the Local Government Board and to the Secretary of State for Scotland. London: Her Majesty's Stationery Office.

This Report, as usual, is replete with interesting matter, both as bearing on public health and on the industrial position of the country.

The total number of works in the United Kingdom, registered under the Act, was at the close of 1888 1057, a decrease of 9 as compared with 1887. The falling off has occurred chiefly in Scotland. In the number of processes under inspection there has been no great change. The larger works seem to be, as a whole, increasing in size, whilst the smaller ones tend to close their operations.

The visits of inspection, in case of works in full activity, are made about once a month, but the intervals are quite irregular. No notice is given, and the escaping gases may be sampled for analysis even in the night.

It is satisfactory to find that in all the districts, save one, the average amount of acid gases escaping falls below one-half of the limit fixed by the Act. In all cases there appears to be a slight, but constantly progressive, improvement.

Prosecution has been found necessary in eight cases, in six of which the offence was neglect of registration.

It is pleasant to find that the inspectors are now regarded by manufacturers by no means in the light of enemies. An eminent manufacturer, Mr. Chance, of Oldbury, said, in a discourse delivered before the Philosophical Society of Birmingham:—"In my opinion Government inspection has not only led to material improvements in the general management of chemical works, but it has been in reality a distinct benefit to, rather than a tax upon, the owners of such works."

As regards the statistics of the alkali trade, an improvement is perceptible as compared with 1887. The quantity of alkali produced by the ammonia process is equivalent to 212,181 tons of salt decomposed, as against 158,636 tons in 1887. Yet, in the face of this advance, the decline in the Leblanc process has ceased, and been succeeded by a revival. The salt consumed in this process was in 1886, 584,323 tons, and in 1887 it had fallen to 577,381 tons; but in 1888 it rose to 590,312 tons. The ammonia-soda makers have not yet succeeded in producing bleaching-powder by their process, and the Leblanc makers, on the other hand, thanks to the inventive skill of Mr. A. M. Chance, of Oldbury, are now able to recover 90 per cent of the sulphur, till lately wasted,—expensively and annoyingly wasted,—in the form of tank waste. The recovered sulphur fetches the highest price of any in the market, and will, it is hoped, compete seriously with Sicilian sulphur.

The processes of Messrs. Parnell and Simpson, and of Mr. F. Gossage, are likewise very promising. The former will recover the sulphur from the waste, whilst the latter seems likely to prevent its future formation.

The maintenance of the Leblanc process is of no small national importance, since, though soda is being abundantly and profitably made in Britain by the rival method, yet we have about £3,000,000 of capital sunk in plant which would be of little, if any, use for other purposes.

The quantity of ammonia produced in the country in the form of sulphate is steadily increasing, and has now reached 122,785 tons, as against 113,896 tons in 1887. Its value is upwards of £1,400,000 yearly.

The subject of black coal-smoke, though not in itself falling within the provisions of the Act, has been brought under the notice of the Inspector in consequence of a report which had gained credence in Manchester and elsewhere that black smoke is a guarantee for the absence of the deadly carbon monoxide. A chemist would at once perceive the absurdity of this view, which was actually brought forward in a court of law as a plea in mitigation of the penalty incurred for the production of black smoke. For the benefit of the non-chemical public the Inspector had the combustion gases from a number of chimneys analysed. Carbon monoxide was not often found, but when it occurred it was always in company with black smoke. "In every case where the black smoke is absent this gas is absent also."

There are hopes that the "thermo-motor" devised by

Mr. Hargreaves may cut away altogether the causes of the smoke nuisance. A 40 horse-power engine on this principle is already in successful operation.

Mr. Mond's system of using gaseous fuel is also of high promise, since it not merely gives a smokeless sootless fire, but saves the ammonia which in other systems is wasted.

In the separate report addressed to the Secretary of State for Scotland there is reference in speaking of tank-waste to an abomination which, I fear, is increasing. At one of the Scottish alkali works it has become the practice to convey the waste in barges to the entrance of Loch Long and there discharge it. The result was great dissatisfaction on the part of residents on the shores of the Loch and of the fishermen. The Inspector found that the Alkali Act did not give him the power to interfere. On remonstance, however, the proprietors of the works discontinued the practice. The greater importance attaches to this matter, since it proposed to convey the sewage-sludge of London out to sea, and deposit it there.

The Inspector points out, as he did in the Report for 1887, certain grave anomalies and inconsistences which greatly interfere with the working of the Act. He proposes the following schedule of substances, the escape of which should be put under restriction :—"The acid compounds of chlorine, fluorine, sulphur, and nitrogen chlorine, and metallic fumes." We should suggest in place of "the acid compounds," all "volatile compounds."

The Report before us will doubtless satisfy all competent judges of the thorough efficiency of the Inspectors.

Electro-Metallurgy, Practically Treated. By Alexander Watt. Ninth Edition, Enlarged and Revised, with additional Illustrations and including the most Recent Processes. London: Crosby Lockwood and Son.

This volume forms one of "Weale's Rudimentary Series," issued by the eminent firm of technological publishers whose name we find on the title-page. Concerning a work which has reached its ninth edition little can be said by the reviewer, since, if it did not meet the requirements of a large number of persons it would by this time have dropped out of notice.

The author touches upon the difficult question of removing the tin from tinners' waste. On this subject not a few inventors have tried their skill, some using purely chemical and some electrical processes. The author doubts, however, and that not without reason, whether any of them have met with absolute success. It is required to obtain the tin absolutely free from iron, and the residual iron as free from tin, and to effect this separation "at a price." We believe that a company has been formed not long ago for working one of the new methods of separation on the large scale, but we do not know whether it has been successful.

The author gives a process for the preparation of potassium cyanide. We scarcely think that an electro-metallurgist, unless his operations are conducted on a very large scale, will find any advantage in producing cyanide for his own use. The same caution applies still more forcibly to the preparation of caustic soda and potassa, both of which may now be bought in small quantities.

We find from this work that according to a reprehensible trade usage articles manufactured from gold and "metal," united and rolled out into thin sheets, are spoken of as "fine gold." The author advises the electro-gilder to make himself acquainted with the various kinds of spurious gold occurring in commerce. He once placed two "gold" Albert chains in a jar of nitric acid, and, on returning in an hour to the gilding room, he found that the chains had disappeared except a thin shell of one of the links and a dark brown powder at the bottom of the jar. These chains, which had been invoiced at 55s. 6d. each, wholesale price, were merely plated metal!

A fact not generally known and here mentioned is that potassium cyanide has a very destructive action upon gutta-percha.

As the applications of electricity in metallurgy are extending this volume is likely to prove of increasing interest.

The Chemistry of the Coal-tar Colours. Translated from the German of Dr. R. Benedikt, and Edited, with Additions by E. Knecht, Ph.D., F.I.C., Head Master of the Chemistry and Dyeing Department of the Technical College, Bradford; Editor of the *Journal of the Society of Dyers and Colourists.* Second Edition, revised and enlarged. London: G. Bell and Sons.

That a second edition of this book has been called for within three years is doubly satisfactory, proving, on the one hand the value of the work, and on the other the increase of an intelligent interest felt in the scientific principles of the industrial arts.

The present edition has been greatly extended. This change is in part necessitated by the discovery of a number of new colours. If we compare the index of the first edition with that of the present volume we shall see that this increase is considerable. The author, however, is of opinion that "of all the artificial dye-stuffs at present in use there are, perhaps, only a few, especially those which are distinguished by their superior fastness, that will maintain a permanent position in dyeing."

The author evidently does not agree with the school of neo-esthetics—shall we say pseudo-esthetics?—who admire impure colours. It must be admitted, however, that the pure colours now being obtained by refined chemical procedures require much greater judgment to bring them into harmonious combinations than do the "subdued" shades which are at present so much in fashion. It has even been suggested that our sense-perceptions are entering upon a process of degradation; witness the rage for bitter flavours, for Wagnerian music, and for the "modes" and terra-cottas which are everywhere encountered.

We have hopes that Dr. Knecht's book will aid in bringing a much-needed reform, both in the manufacture of dyes in this country, and in their application. But after all, until examinationism and "payment by results" are dethroned in our colleges and technical schools we shall be more fruitful in men who can talk about processes and results than in those who can bring them to pass.

The Retrospect of Medicine: A Half-yearly Journal, containing a Retrospective View of every Discovery and Practical Improvement in the Medical Sciences. Edited by James Braithwaite, M.D. (Lond). Vol. xcix., January to June, 1889. London: Simpkin, Marshall, and Co.

This issue contains but little matter of which we can presume to take cognisance. Creoline—a coal product—seems to be attracting notice as a germicide. It is found to be a stronger antiseptic than carbolic acid, and as a deodorising agent it is better than either carbolic acid or mercuric chloride.

Dr. Raudnitz recommends the sterilisation of milk at the time of milking. Such milk, after being kept at the ordinary temperature of a room for three weeks, remained alkaline, and could not be distinguished from freshly drawn milk either by taste, odour, or appearance. Since Dr. Raudnitz introduced it among his patients he has seen no cases of diarrhœa.

In a paper on lead-poisoning, of which several cases have lately occurred in the North of England, Mr. Norman Porrit concludes that alcohol has a very powerful effect in intensifying the effects of lead.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 3, July 15, 1889.

Thermic Researches on the Isomeric Nitro-camphors and on Cyano-camphor. — M. Berthelot and P. Petit.—The authors investigate the thermo-chemical signification of the camphenic derivatives, especially as regards the isomeric nitro-compounds, the function of which is connected on the one hand with the nitric ethers of the fatty series, properly so-called, and on the other to the nitro-phenols of the aromatic series.

The Reactions of the Oils with Silver Nitrate.—Raoul Brullé.—If we treat 10 c.c. of an oil with 0·5 c.c. of fuming nitric acid in a porcelain capsule and heat the mixture with brisk stirring until froth appears, different colourations are produced according to the oil used. The treatment is continued, adding 5 c.c. of a solution of silver nitrate at 2½ per cent in alcohol at 90 per cent. If we continue heating there comes a moment, about 115°, when the silver nitrate is suddenly decomposed and metallic silver is deposited. We continue heating so as to let the first reflections disappear, and we observe on the sides of the capsule the colour of the thin oily layer seen on inclining the capsule and the metallic reflections on the surface of the liquid. On saponifying the oils and treating them in the same manner we obtain quite different colours, as obtained in the table:—

1. *In the Natural State.*

Oil.	Oily Layer.	Reflection.
Olive.	Olive green.	Green.
Cotton.	Green.	Ash green.
Sesame.	Chrome green.	Light Sèvres blue.
Earthnut.	Yellowish green.	Emerald green.
Camelina.	Persian lake.	Light blue.
Linseed.	Dragon's blood.	Emerald green.
Colza.	Persian lake.	Cyprus green.

2. *When Saponified.*

Oil.	Oily Layer.	Reflection.
Olive.	Mars orange.	Cyprus green.
Cotton.	Terra di Sienna.	Cobalt violet.
Sesame.	Gold yellow.	Cobalt violet.
Earthnut.	Persian lake.	Light violet.
Camelina.	Deep chrome.	Blue.
Linseed.	Black.	Green.
Colza.	Burnt carmine.	Ultramarine.

The names of the colours are those used by artists in water-colours.

The Decomposition of the Sulpho-conjugated Acids by Means of Phosphoric Acid.—C. Friedel and J. M. Crafts.—The former processes for the regeneration of an aromatic hydrocarbon from its sulpho-conjugated compound turned on the action of hydrochloric acid, or, as proposed by Messrs. Armstrong and Miller, of sulphuric acid in a current of steam at 170°. The authors, after explaining the defects of both these methods, propose to mix the sodium or potassium salt of a sulphuric acid with a considerable excess of phosphoric acid at 60° B.

On the Brownian Movement.—M. Gouy.—The author concludes that the pedetic movement is the only physical phenomenon which renders visible a constant internal state of agitation in bodies in the absence of any outward cause.

The Electrolysis of Distilled Water.—E. Duter.—This paper will be inserted in full.

On the Ammonio-cobaltic Molybdates, Tungstates, and Vanadiates. Separation of Cobalt and Nickel and of the Cobaltous and Cobaltic Salts.—Adolphe Carnot.—(See p. 54).

New Derivatives of Camphor.—A. Haller.—This paper does not admit of useful abstraction.

The Simultaneous Determination of Saccharose and Raffinose in Commercial Products.—L. Lindet.—This memoir also cannot be abridged.

Journal fur Praktische Chemie.
Vol. xxxix., Parts 8 and 9, 1889.

Researches from the Laboratory of the University of Freiburg.—These include papers on tolunitranilic acid and some derivatives of hydrotoluquinone, by Fr. Kehrmann and R. Brasch; on iodophenolsulphonic acid and iodoquinon by Fr. Kehrmann; and on chlorobromo-paraxylols and some of their derivatives by C. Willgerodt and R. Wolfien.

Contributions to a Knowledge of the Modifications of Cadmium Sulphide produced in the Moist Way.—N. von Klobukow.—Cadmium sulphide obtained in the moist way varies in colour from a light yellow to a deep reddish brown. Formerly the differences of colour and the modifications in density were ascribed to a difference in chemical composition. It appears, however, from the comprehensive investigations of Follenius and Buchner that in aqueous solutions of cadmium there is formed only one grade of sulphuration, cadmium monosulphide, and that the precipitates of different colours have the same empirical composition. The author concludes that the determination of the sp. gr. of the modifications of cadmium sulphide described by Buchner speaks in favour of their isomeric character. Crystallographic examination leads to the same result, and renders it probable that there exist more than two modifications of cadmium sulphide. The mutual transformation of the modifications of cadmium sulphide can be effected not merely by the action of heat and of various chemical agents, but by friction, pressure, and by means of nascent hydrogen.

On the Fission-products of Casein.—E. Drechsel.—In this preliminary notice the author raises the questions:—If all the albumenoids, on treatment with strong hydrochloric acid, yield identical bases, do animal and vegetal albumenoids behave identically or not? What is the relation of these bases to the ptomaines?

Researches from the Laboratory of Prof. Saytzeff at Kasan.—These researches comprise:—Action of iodmethyl and zinc upon ethyl-propyl-keton, by E. Sokoloff; action of iodethyl and zinc upon ethyl-propyl-keton, by E. Sokoloff; examination of the hydrocarbons C_8H_{16} and C_9H_{18} from methyl-dipropyl-carbinol and ethyl-dipropyl-carbinol, by E. Sokoloff; action of iodethyl and zinc upon malonic ethyl-ether, by St. Joukowsky; action of iodallyl and zinc upon malonic ethyl-ether, by W. Matweeff.

On Certain Ferrocyanides.—C. Rammelsberg.—The author describes lead ferrocyanide with the modifications obtained by Zepharovich, Gintl, and Wyrouboff, barium, hydrogen, and silver ferrocyanides.

Libel on a Chemist.—The Press of Paris, and in particular the *XIX Siècle*, have lately brought against M. Charles Girard, the Director of the Municipal Laboratory, charges of incapacity and of accepting bribes. Girard, in consequence, took proceedings for libel. The editor of the *XIX Siècle* has been condemned to one month's imprisonment, a penalty of 1000 francs, and to pay the plaintiff 15,000 francs damages.—*Chemiker Zeitung.*

THE CHEMICAL NEWS.

Vol. LX. No. 1550.

ON RECENT RESEARCHES ON THE RARE EARTHS AS INTERPRETED BY THE SPECTROSCOPE.*

By WILLIAM CROOKES, F.R.S., &c.

(Concluded from p. 53).

Action of Different Earths on Phosphorescence Spectra.

Another modification of phosphorescence spectroscopy is produced by the previous addition of other earths to the specially phosphorescent earths, and of the results of such addition some instances have already been mentioned. Lime exerts in this manner a remarkable action. By itself it phosphoresces with a continuous spectrum, after the fashion of yttria with a discontinuous spectrum. If, however, they are mixed, the phosphorescing energy of the lime does not extend over the whole spectrum, but concentrates itself on strengthening the yttria bands. These bands become broader, but also less definite, in proportion as the lime increases in quantity.

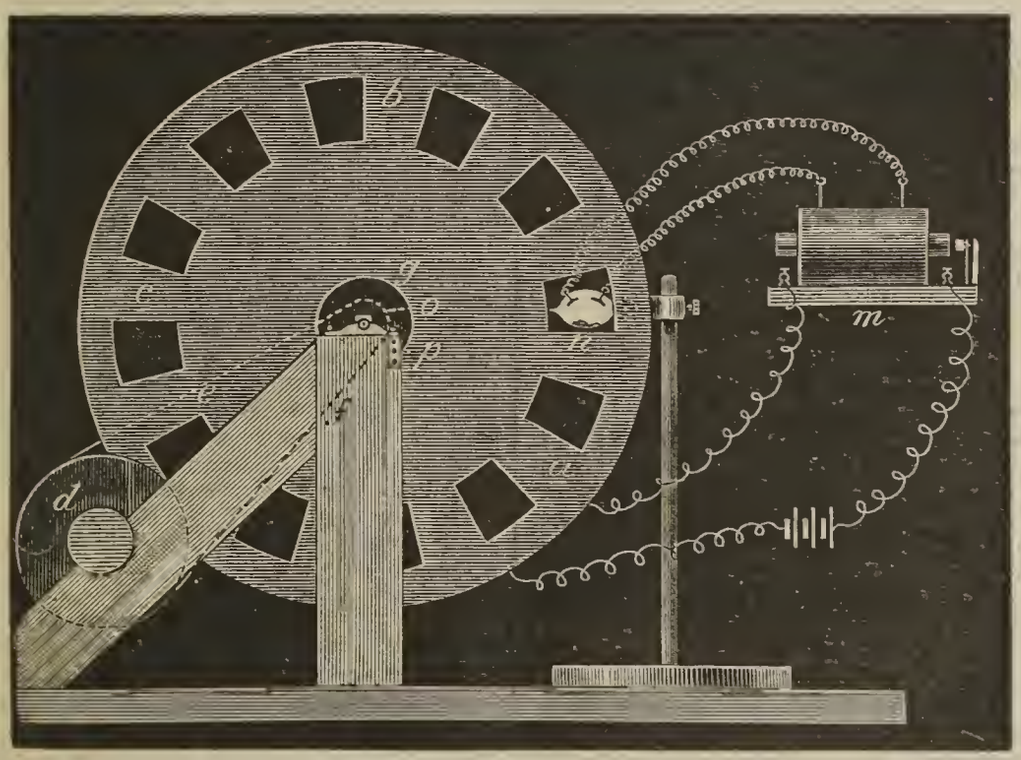
Lime also may be made to play a useful part in bringing out the phosphorescent bands of samaria. The bands are not so numerous as those of yttrium, but the contrasts are sharper. Examined with a somewhat broad slit, and disregarding the fainter bands, the samarium spectrum is seen to consist of three bright bands—red, orange, and green — nearly equidistant, the orange being brightest. With a narrower slit the orange and green bands are seen to be double. (Fig. 18).

The addition of lime also affords an argument for the compound nature of samaria, as it suppresses the sharp line Sδ, the most striking feature in the phosphorescence spectrum shown by pure samarium sulphate. On the other hand, an addition of old yttria deadens the other lines of samaria, but brings out the line Sδ more strongly. Fig. 19 represents the spectra given by the meta-elements of samarium.

Lanthanum sulphate in the radiant matter tube phosphoresces with a reddish colour and has a broad hazy band in the orange, with a sharp line superposed. This line is identical with the line of Gε, one of the components of the phosphorescent spectrum of samarium. If lime is added to lanthanum, the phosphorescence changes its colour from red to yellow. Lime also brings out the lines of yttrium and samarium if they are present as impurities. When Gδ, Gα, and Gβ are present in small proportions with lime, the lines Gδ and Gα become intensified, but a dark place appears in place of the green Gβ band. Hence it appears that if only a small trace of Gβ is found with lime and lanthanum, the green line is not only obliterated, but the quenching action suppresses that part of the continuous lime spectrum which has the same refrangibility as the Gβ line, thus giving a black space in the spectrum.

A specimen of lanthana thrown out in a fractionation of didymia, examined in the radiant matter tube, phosphoresces of a yellow surface-colour and gives an extremely brilliant spectrum (Fig. 20). In the red there is a very fine and sharp line, somewhat like the alumina line, but nearer C of hydrogen. Then come a couple of misty red lines, the first apparently compound, then a hazy pair of green lines, and finally another wide apart pair of a bluish green; the first of these lines is intensely brilliant.

Fig. 22.



Interference of Phosphorescence Spectra.

I have already frequently noted the modification induced in the normal spectrum of one earth by the mixture of various quantities of others, when treated as anhydrous sulphates, and of these one of the most striking is seen in the case of a mixture of samaria with yttria, since the presence of even 40 per cent of yttria practically obliterates its spectrum. The most minute proportion of

* Address delivered by the President of the Chemical Society at the Annual General Meeting, March 21st, 1889.

lime added to samaria causes the sharp line at $1/\lambda^2$ 269 in its spectrum to vanish, at the same time greatly intensifying the other bands. Strontia, baryta, glucina, thoria, magnesia, lanthana, alumina, and oxides of zinc, cadmium, lead, bismuth, and antimony, all give characteristic spectra with samaria, and have been fully described in my paper on that body (*Phil. Trans.*, Part II., 1885). The action of lime upon yttria is of great use in detecting very small quantities of this earth when in combination with other elements which otherwise would prevent its phosphorescence.

A recent discovery of some beautiful spectra given by the rare earths when their pure oxides are highly calcined, shows the remarkable changes produced in the spectra of these earths when two or more are observed in combination. It has likewise opened to me a wide field of investigation in the nature of the elements themselves. Alumina is especially active in inducing new spectra when mixed with the rare earths. I have given more than a twelvemonth to the exclusive study of alumina phosphorescence, and still the research is incomplete. But I have obtained some remarkable results. A moderate amount of fractionation has enabled me to penetrate below the surface of the red glow common to crude alumina, and to see traces of a most complicated sharp line spectrum. By pushing one particular process of fractionation to a considerable extent, I have obtained evidence of a body which is the cause of some of these lines. The spectrum described by me in 1887 (CHEM. NEWS, lvi., 62, 72) is one of great beauty, and a fair idea of it is given in Fig. 21. The new body is probably one of the rare elements or meta-elements closely connected with decipia, for I have reproduced the spectrum very fairly by adding decipia to alumina. Before arriving at definite conclusions much time must be devoted to the subject. Certain it is that this new earth is not yttria, erbia, samaria, didymia, lanthana, holmia, thulia, gadolinia, or ytterbia, the spectrum of each of these when mixed with alumina being very beautiful, but differing entirely from the decipia-alumina spectrum. Some of these new spectra are shown in Fig. 29.

The Phosphoroscope.

The phosphoroscope affords another method of verifying the simple or compound character of a substance. It is well known that the continuance of phosphorescence after the cessation of the exciting cause varies widely, from some hours, as in the case of the phosphorescent sulphides, to the fraction of a second in the case of uranium glass and quinine sulphate. On examining phosphorescent earths glowing in a vacuum tube under the action of the induction discharge, I found remarkable differences in the duration of this residual glow. Some of the earths, after the cessation of the current, remain luminous for an hour or more, whilst others cease to phosphoresce immediately on the stoppage of the current. Take the case of yttrium. As already stated, I succeeded in resolving this earth into several simpler bodies not equal in basicity. While seeking for further proof of the distinct character of these bodies I observed that the after-glow differed somewhat in colour from that which the earth exhibited whilst the current was still passing. Further, the spectrum of the after-glow seemed to show, so far as I could judge by the faint light, that some of the lines were missing. As this phenomenon indicated another difference among the components of yttrium, I examined them in an instrument similar to Becquerel's phosphoroscope, but acting electrically instead of by means of direct light.

Without describing this apparatus, shown in Fig. 22, I may mention some of the results obtained by its use. Under ordinary circumstances it is scarcely possible to perceive any phosphorescence in an earth until the vacuum is so high that the line spectrum of the residual gas begins to grow faint. Up to this point, the stronger light of the glowing gas overpowers the feeble glow of the phosphorescence. But in the phosphoroscope the light of the glowing gas lasts only for an inappreciable time, while that of the phosphorescent earth persists long enough to be distinctly observed. The different bands of the new constituents of yttria do not all appear at the same speed of rotation. At the lowest speed the double greenish blue band of $G\beta$ is first seen, followed next by the dark blue band of $G\alpha$. As the velocity increases there follows the bright citron-yellow band of $G\delta$, and as the utmost speed approaches the red band of $G\zeta$ is seen, but with difficulty. If lanthanum sulphate along with a little lime is examined in the phosphoroscope the line of $G\varepsilon$ is visible at the lowest speed; $G\delta$ follows at an interval of 0·0035 second, and the $G\alpha$ line immediately afterwards.

M. de Boisbaudran's Reversion Spectra.

Another modification of the phosphorescence process is afforded by the "reversion spectra" of M. Lecoq de Boisbaudran.

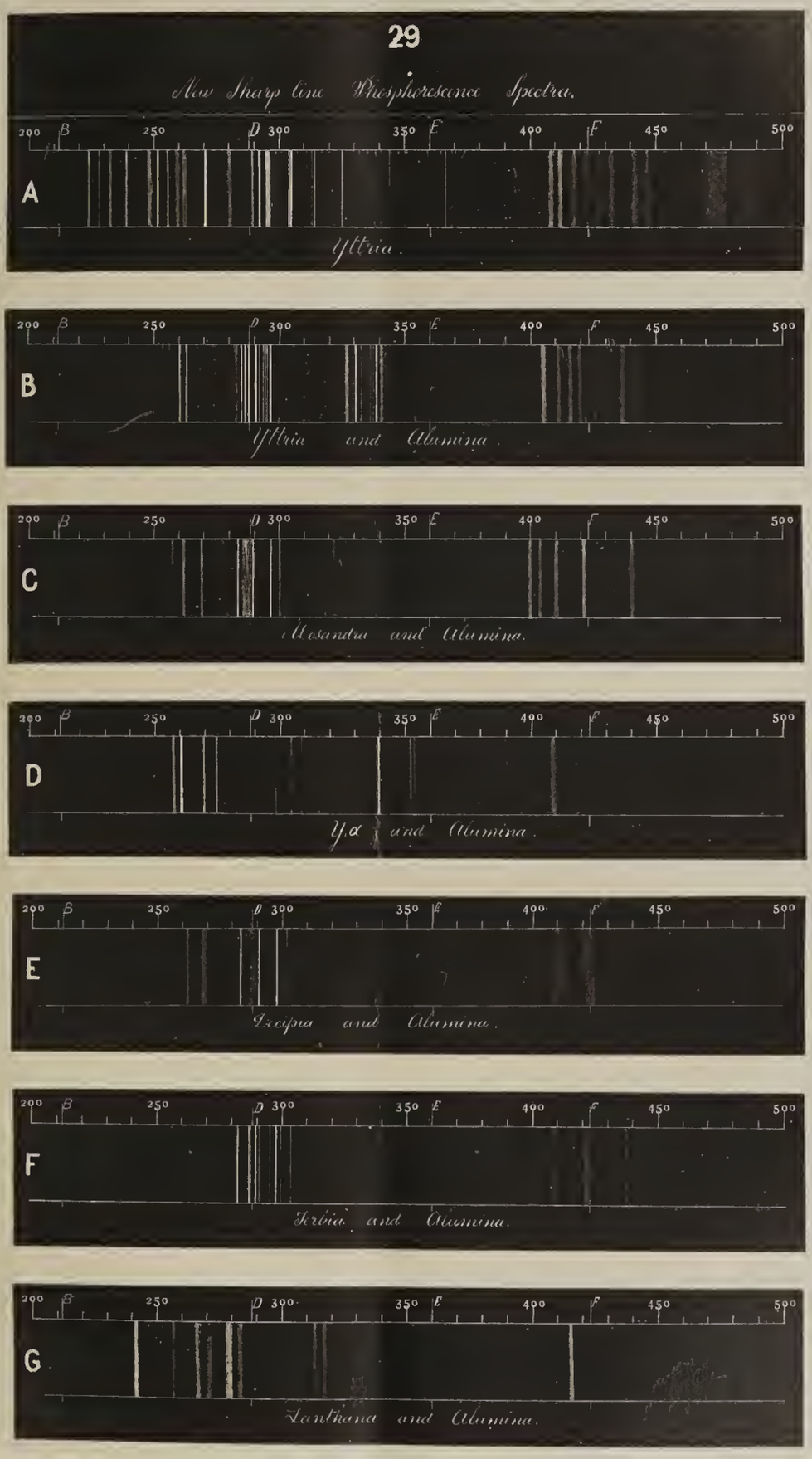
The following is the description of this process by M. Lecoq de Boisbaudran, read before the Academy of Sciences on June 8th, 1885:—"When the electric spectrum of a solution *with a metallic base* is produced it is customary to make the outside platinum wire (whence the induction spark strikes) positive, the liquid consequently forming the negative pole. If the direction of the current is reversed the metallic rays (due to the free metal or to one of its compounds) are scarcely or not at all visible; at all events, so long as the exterior platinum wire now forming the negative pole is not coated with a deposit." Fig. 15 shows the arrangement. M. de Boisbaudran continues:—

"Having again taken up last year my researches on the rare earths belonging to the didymium and yttrium family, I had occasion to observe with many of my preparations the formation of spectrum bands, nebulous, but sometimes tolerably brilliant, having their origin in a thin layer of a beautiful green colour, which appeared at the surface of the liquid (a solution of a chloride) when it was rendered positive."

M. de Boisbaudran further adds:—"The production of my reversion spectrum appears to be analogous physically with the formation of the phosphorescence spectra obtained by Mr. Crookes at the negative pole in his high vacuum tubes containing certain compounds of yttria. The conditions of the two experiments are, however, practically speaking, very different."

By this method M. de Boisbaudran has discovered phosphorescent spectra, shown in Figs. 23 and 24, which he considers due to the presence of two earths, one of which, supposed to be new, he has provisionally named $Z\alpha$, and another, also thought at first to be new, and therefore called $Z\beta$, but since admitted by him to be terbia (*Compt. Rend.*, cviii., 167, Jan. 28, 1889). In the hands of so skilful an experimentalist as my accomplished friend, this method may give trustworthy indications, but the test is really beyond the range of practical analysis, owing to the difficulty of eliciting the phenomena. Unless the strength of the spark, the concentration and acidity of the solution, and the dispersive and magnifying power of the spectroscope bear a certain proportion to each other, the observer is likely to fail in seeing a spectrum even in solutions of earths which contain considerable quantities of $Z\alpha$ and terbia.

I have had not only the advantage of personal instruction in Paris from M. de Boisbaudran himself in the best methods of getting these reversion spectra, but I secured some of the identical earths which give these spectra most distinctly. Yet with all these advantages I have experimented for hours together without being able to see more than a feeble glimmer of the bands described by M. de Boisbaudran. Moreover, the bands of these "reversion" spectra, at their strongest, are but faint and hazy substitutes for the brilliant lines of yttria seen by the "bombardment" process, and they do not even in all cases agree with them in position. M. de Boisbaudran,



SPECTROSCOPIC RESEARCHES ON THE RARE EARTHS.
W. CROOKES.

speaking of the relative sensitiveness of our two processes, admits that the bombardment process *in vacuo* is incomparably more delicate than his reversion method. My own estimate of the relative sensitiveness of the two methods is in the proportion of at least 1 : 100. Though so accurate an observer, M. de Boisbaudran concluded apparently too hastily that two spectra are identical, when one of them has been measured only approximately, and contains bands in positions which are perfectly blank in the other.

The Phosphorescence of Alumina.

I now wish to draw attention to some recent researches on the phosphorescence spectrum given by alumina. So far back as 1859 Becquerel examined in his phosphoroscope pure alumina carefully prepared, and described it as glowing with a splendid red colour. He rendered his specimens phosphorescent by exposure to the sun, and made no use of the induction spark. As described by Becquerel (*Ann. Chem. Phys.*, lvii., 50, 1859), the spectrum of the red light emitted from alumina agrees with that of the ruby when submitted to the radiant matter test. It displays one intensely red line a little below the fixed line B in the spectrum, having a wave-length of about 689·5. There is a continuous spectrum beginning at about B and a few fainter lines beyond it, but in comparison with this red line the faint ones are so dim that they may be neglected. My latest observations in the vacuum tube prove this line to be double, the distance apart of the components being about half the distance separating the D lines (*Proc. Roy. Soc.*, xlii., 26, Dec. 30, 1886), their respective wave-lengths being 694·2 and 693·7 ($1/\lambda^2$ 207·5 and 207·8). This alumina spectrum is shown in Fig. 25.

The red phosphorescence of this alumina is exceedingly characteristic. M. de Boisbaudran (*Compt. Rend.*, ciii., 1107; civ., 330, 478, 554, 824) contends, however, that this red phosphorescence is due not to the alumina itself, but to an accompanying trace of chromium, $\frac{1}{1000}$th part of chromium being sufficient to give a splendid red phosphorescence, whilst even 1 part of chromic oxide in 10,000 will produce a very distinct rose colour. In testing this view I have purified alumina most carefully, so as to secure the absence of chromium, and on examining it in the radiant matter tube I have still obtained the characteristic phosphorescence and spectrum. I have then added to my purified alumina chromium in known varying proportions, but without finding any increase in the intensity of the phosphorescence. I fractionated my purified alumina by different methods and found that the substance which forms the crimson line becomes concentrated towards one end of the fractionations, whilst chromium concentrates at the other end. I have suggested four possible explanations of the phenomena—

1. The crimson line belongs to alumina, but it is liable to be masked or extinguished by some other earth, which accumulates towards one end of the fractionations.

2. The crimson line is not due to alumina, but to the presence of an accompanying earth, which accumulates towards the other end of the fractionations.

3. The crimson line belongs to alumina, but its development requires certain precautions to be taken in the duration and intensity of the ignition, and absolute freedom from alkaline and other bodies carried down by precipitated alumina, and difficult of removal by washing.

4. The earth alumina is a compound molecule, one only of its component sub-molecules giving the crimson line. If this hypothesis is correct, alumina must admit of being split up in a manner analogous to yttria.

Sharp Line Spectra with Phosphorescent Alumina.

About eighteen months ago M. de Boisbaudran published some results on "New Fluorescence with well-defined Spectral Rays" (*Compt. Rend.*, cv., 258). Having mixed alumina with 2 per cent of samaria and converted the mixture into sulphate, he heated it to a temperature between the melting-point of copper and silver. This product, examined in the radiant matter tube, gives a faint fluorescence, the spectrum resembling the samarium-aluminium spectrum described by me in June, 1885 (*Phil. Trans.*, Part II., 1885, 712) (Fig. 26). That is, aluminium and samarium give a spectrum resembling the corresponding calcium-samarium one as to the red and the double orange, but having a very broad, rather faint, green band with a black division in the middle occupying the position of the bright green band of calcium-samarium.

On submitting this aluminium-samarium mixture to a very high temperature, M. de Boisbaudran finds that its spectrum alters greatly. In place of the three nebulous bands, there are now a number of sharp rays forming three groups corresponding respectively to each of the three diffused bands above described.

This spectrum seems to me closely to resemble the complicated system of sharp lines shown by alumina after moderate fractionation, to which I have already referred (Fig. 27, lower spectrum). Taking some of this alumina, I added to it one-fiftieth of its weight of samaria, and thereby obtained a spectrum similar to that described by M. de Boisbaudran (Fig. 27, upper spectrum). As I had suspected, the two spectra are almost identical; the effect of the samaria is simply to intensify some of the lines and weaken others. But between this sharp line high temperature spectrum and the band spectrum (Fig. 26) given by the same mixture treated at a lower temperature I fail to see any such resemblance as could support the view that the groups correspond save that "those of the line spectra are less refrangible." The explanation of M. de Boisbaudran's result is simple. Both samarium sulphate and aluminium sulphate resist a red heat without their sulphuric acid being driven off. Aluminium sulphate does not phosphoresce, samarium sulphate does, therefore the mixture gives the samarium spectrum. But if the mixed sulphates are heated to the highest blowpipe temperature both are decomposed, and there is left a mixture of samaria and alumina. Now, samaria by itself gives no phosphorescence spectrum, but alumina gives the new line spectrum I have described.

This method is applicable only when the earths are in a sufficiently high state of purity. The presence of exceedingly small traces of other matter may greatly modify the spectrum.

Conclusions.

During the course of the investigations—whose results are briefly summarised in the foregoing pages,—I have repeatedly had recourse to the balance, to ascertain how the atomic weights of the earths under treatment were varying. An atomic weight determination is valuable in telling when a stable molecular grouping is arrived at. During a fractionation, the atomic weight of the earth slowly rises or falls until it becomes stationary, after which no further fractionation of that lot *by the same process* makes it vary. Usually a result of this kind has been relied on as proof that the elementary stage has been reached. This constancy of atomic weight, however, only proves that the original body has been split up by the fractionating process into two molecular groupings capable of resisting further decomposition by that identical process; but these groupings are not unlikely to break up when a different fractionating process is brought to bear on them, as I found in the separation of didymium and samarium when using dilute ammonia as the fractionating precipitant. In my paper on "Radiant Matter Spectroscopy" I said*:—"After a time a balance seems to be established between the affinities at work, when the earth would appear in the same proportion in the precipitate and the solution. At this stage they were thrown down by ammonia, and the precipitated earths set aside to be worked up by the fusion of their anhydrous nitrates so as to alter the ratio between them,

* Part II., Samarium," *Phil. Trans.*, Part II., 129, June 18, 1885.

when fractionation by ammonia could be again employed."

It is obvious that when the balance of affinities here spoken of was reached, the atomic weight of the mixture under treatment would have become constant, and no further fractionation would have caused the atomic weight to alter.

Atomic weight determinations are valuable in telling when the fractionating operation in use has effected all the separation it can: at this point it becomes constant. The true inference is, not that a new earth has been obtained, but simply that the fractionating operation requires changing for another, which will cleave the group of meta-elements in a different direction.

Meantime, I have kept strictly in view the question, What is an element, and how shall it be recognised when met?

On this subject I beg to submit the following considerations, which, primarily referring to didymium, may at any moment apply to other cases:—

Neodymium and praseodymium are simply the products into which didymium is split up by one particular method of attack.

It must be remembered that a single operation, be it crystallisation, precipitation, fusion, partial solution, &c., can only separate a mixture of several bodies into two parts, just as the addition of a reagent only divides a mixture into two portions, a precipitate and a solution, and these divisions will be effected on different lines according to the reagent employed. We add, *e.g.* ammonia to a mixture, and at once get a separation into two parts. Or we add, say, oxalic acid to the same original solution, and we then split up the mixture into two other parts differently arranged.

Thus by crystallising didymium nitrate (in Auer's way) we divide the components into two parts. By fusing didymium nitrate we divide its components in a different way; but so long as different methods of attack split up a body differently, it is evident that we have not yet got down to "bed rock."

Further, a compound molecule may easily act as an element. Take the case of didymium, which is certainly a compound, whether the products of Auer's operation be final or not. Didymium has a definite atomic weight; it has well-defined salts, and has been subjected to the closest scrutiny by some of the ablest chemists in the world. I refer particularly to Clève's classical memoir. Still the compound molecule known as didymium was first too firmly held together to act otherwise than as an element, and as a seeming element it emerged from every trial. The simple operations to which it had been submitted in the preparation of its salts, and in its purification from other compound molecules, such as samarium and lanthanum, were not sufficient to split it up further. But subjected to a new method of attack it decomposes at once.

We have, in fact, a certain number of reagents, operations, processes, &c., in use. If a body resist all these and behave otherwise as a simple substance, we are apt to take it at its own valuation, and to call it an element. But for all that, it may, as we see, be compound, and as soon as a new and appropriate method of attack is devised we find it can be split up with comparative ease. Still, we must never forget that, however complex, it can hardly be resolved into more than two parts at one operation.

From considerations above laid down I do not feel in a position to recognise neodymium and praseodymium as elements. We need some criterion for an element which shall appeal to our reason more clearly than the old untrustworthy characteristic of having not as yet been decomposed, and to this point I must beg to call the special attention of my colleagues. It may be that whatever body gives only one absorption-band is an element, but we cannot conversely say that an element may be known by its giving only one absorption-band, since most of our elements give no bands at all!

Until these important and difficult questions can be decided, I have preferred to open what may be figuratively called a suspense account, wherein, as I have previously suggested, we may provisionally enter all these doubtful bodies as "meta-elements."

But these meta-elements may have more than a mere provisional value. Besides compounds, we have hitherto recognised merely ultimate atoms, or the aggregations of such atoms into simple molecules. But it becomes more and more probable that between the atom and the compound we have a gradation of molecules of different ranks, which, as we have seen, may pass for simple elementary bodies. It might be the easier plan, so soon as a constituent of these earths can be found to be chemically and spectroscopically distinguishable from its next of kin to give it a name, and to claim for it elemental rank; but it seems to me the duty of a man of science to treat every subject, not in the manner which may earn for him the greatest temporary κυδος, but in that which will be of most service to Science.

If the study of the rare earths leads us to clearer views on the nature of the elements, neither my colleagues nor myself will, I am sure, regret the months spent in tedious and apparently wearisome fractionations. No one can be more conscious than myself how much ground is yet uncovered, and how many radical questions have received but very inadequate answers. But we can only work on, "unresting, unhasting," trusting that in the end our work will throw some white light upon this deeply interesting department of chemical physics.

THE MOLECULAR WEIGHTS OF SOME POLYMERIC COMPOUNDS AS DETERMINED BY RAOULT'S METHOD.

By RAPHAEL MELDOLA, F.R.S., and F. W. STREATFEILD, F.I.C.

In the course of some investigations upon the diazoamido-compounds we have recently had occasion to determine the molecular weights of some compounds which, on purely chemical grounds, we had undoubted evidence to show consisted of molecules having double the weight usually assigned. Notwithstanding the chemical evidence, which will be given in a future communication, the molecular weights, as determined by Raoult's method, came out one-half the value required by our formulæ. A precisely similar experience has recently been recorded by Anschütz (*Ber.*, 1889, p. 980) with respect to the dimethyl-ether of diacetylracemic acid. It became of interest, therefore, to examine into the method itself with a view to ascertaining how far it was applicable to the determination of the molecular weights of polymerides. Since this subject has of late excited a great deal of interest, we are induced to make known our results as a contribution to the discussion. The compounds with which we have experimented are aldehyde, paraldehyde, and metaldehyde. The first solvent tried was benzene, because this is the solvent which we had actually to employ for the diazoamides. A specimen of perfectly pure benzene was kindly supplied for our purpose by Messrs. Read Holliday and Sons, of Huddersfield. The method of working the process, and the form of apparatus, are now well known, and require no special description. The usual symbols have been adopted, viz.:—

E, for the observed "setting point" of the solution; the thermometer scale being read off by means of a cathetometer.

C, for the *depression* of freezing-point.

A, for the "coefficient of depression," *i.e.*, the depression of freezing-point produced by 1 grm. of the substance in 100 grms. of the solvent.

M, for the molecular weight calculated from the foregoing values.

I. *Aldehyde*, C_2H_4O, Mol. Wt. 44.

Freezing-point of benzene 5·30, strength of solution 0·4169 grm. aldehyd in 61·81 grms. solvent.*

E.	C.	A.	M.
4·70	0·60	0·889	55
4·70	0·60	0·889	55

Added 0·3710 grm.; total 0·7879 grm.

E.	C.	A.	M.
4·15	1·15	0·902	54
4·15	1·15	0·902	54

Added 0·2239 grm.; total 1·10118 grms.

E.	C.	A.	M.
3·90	1·40	0·855	57
3·90	1·40	0·855	57

II. *Paraldehyde in Benzene*, Mol. Wt. 132.

Freezing-point of benzene 5·3, strength of solution 0·5819 paraldehyde in 66 grms. solvent.

E.	C.	A.	M.
4·98	0·32	0·363	135
4·98	0·32	0·363	135

Added 0·7462 grm.; total 1·3281 grms.

E.	C.	A.	M.
4·53	0·77	0·383	128
4·53	0·77	0·383	128

Added 0·8544 grm.; total 2·1825 grms.

E.	C.	A.	M.
4·05	1·25	0·378	129·6
4·05	1·25	0·378	129·6

Metaldehyde is practically insoluble in benzene, but soluble to some extent in acetic acid, so experiments were next conducted with this solvent.

III. *Paraldehyde in Acetic Acid.*

Freezing-point of acid 16·0, strength of solution 0·8967 grm. in 79·64 grms. solvent.

E.	C.	A.	M.
15·70	0·30	0·266	146
15·70	0·30	0·266	146

Added 1·179 grms.; total 2·0757 grms.

E.	C.	A.	M.
15·25	0·75	0·288	135
15·27	0·73	0·281	138·7

Added 0·4162 grm.; total 2·4919 grms.

E.	C.	A.	M.
15·10	0·90	0·288	135
15·10	0·90	0·288	135

IV. *Metaldehyde in Acetic Acid.*

Freezing-point of acid 16·0, strength of solution 0·1176 grm. in 63·11 grms. solvent.

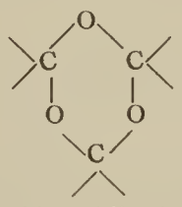
E.	C.	A.	M.
15·90	0·10	0·5366	72·6
15·90	0·10	0·5366	72·6

Metaldehyde is so insoluble in acetic acid that it was not found possible to work with solutions stronger than the above, as the substance crystallised out on cooling down the acid.

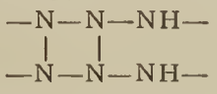
Our experiments have not been conducted with a sufficiently large number of polymeric compounds to warrant any general discussion of the results. As far as they go, it would appear that the method enables us to distinguish between C_2H_4O and $C_6H_{12}O_3$. The results for aldehyde are somewhat high, but it is not certain that the specimen employed, although purchased as pure, may not have contained some polymeride. The result for metaldehyde is abnormal and agrees approximately with—

$$C_2H_4O + \frac{C_2H_4O}{2};$$

mol. wt. 66. Paraldehyde in water gave quite irregular results, probably owing to the chemical action of the solvent. We can fully confirm the statement of Beckmann (*Zeit. f. Phys. Chem.*, ii., 715) that benzene is the solvent which offers the greatest facilities of manipulation. Although the experiments seem to indicate that the molecular weights of polymerides, such as aldehyde and paraldehyde, can be determined by the method of Raoult, we do not think that it is a legitimate deduction to infer that the method is universally applicable to all cases of polymerism. We have, as previously stated, distinct evidence to the contrary with diazoamides, and we may further point to the apparent failure of the method in the case of metaldehyde, which certainly cannot have a smaller molecular weight than paraldehyde. The whole question is, however, complicated by the possible chemical action of acetic acid upon metaldehyde, and we propose to repeat the determination with some other solvent, if a suitable one can be found. There can be but little doubt that in the case of polymerides the stability of the molecule in the solvent determines the success or failure of the method. Thus, paraldehyde may contain the nucleus*:—



which may be fairly stable, while the mixed diazoamides contain the unstable ring†:—



which may easily become broken up in solution.

Finsbury Technical College,
July 20, 1889.

* The aldehyde was weighed in small, thin glass bulbs, which were broken after introduction into the solvent.

* See, for instance, Strecker and Wislicenus, "Text-book of Organic Chemistry," p. 261.

† *Journ. Chem. Soc. Trans.*, 1889, p. 443.

NOTE ON THE ARSENICAL WATER OF COURT ST. ETIENNE (BELGIUM).

By Dr. T. L. PHIPSON, F.C.S., &c., London,
Formerly of the University of Brussels.

In 1872 died J. T. Liboutton, for the previous forty-two years burgomaster of the little town of Court St. Etienne (St. Stephen's Court) in Brabant. He left the greater portion of his fortune to the town in order that an asylum or almshouse for the aged poor might be built there. The authorities set to work without delay, and in the year 1878 the building was completed. It was called, from the name of its founder, the Hospice Liboutton. A very short time elapsed before it was observed that old people appeared to thrive there in a very remarkable manner; the bloom and freshness of youth returned more or less, replacing the dull pale tints of age; and this occurred so rapidly that it seems to have attracted general notice.

In trying to account for this singular fact the management of the Hospice came to the conclusion that it could not possibly be due to any special article of diet, for the food taken was of a very ordinary kind; nor were the

pure air of the locality and dryness of the soil considered sufficient to explain the mystery, for mystery it certainly was, and so it remained until suddenly three of the inmates of the establishment died, at very short intervals, and within six months of the opening of the Hospice. A fourth inmate retired voluntarily from the place, fearing to meet with the same fate as his three companions.

The food, the air, and the soil had been inquired into; at last attention was turned towards the water supplied to the establishment. It was found to be arsenical.

The spring issues near some lodes of mispickel (arsenical iron pyrites), and I find that this water, which is cold, bright, and clear, and has a pleasant taste, yields to analysis 19½ grains of total residue to the imperial gallon. Of these, 0·7 grain is *arsenic acid*, and 0·84 grain ferric oxide, the remainder being composed of the usual compounds of lime, soda, silica, and magnesia, found in spring waters. It is supposed to have a constant composition, but to establish this fact it will be necessary to make another analysis at some distant date. Nevertheless it is supplied to various pharmacies, and is used in medicine as a substitute for Fowler's solution or Bourboule water from the Puy de Dôme (France). It is much richer in arsenic than the water of Mont Dore (Puy de Dôme).

Such is, in a few words, the history of the most recently discovered arsenical mineral spring. The composition of this water and the geological nature of the district—not far from the celebrated plains of Waterloo—do not indicate the most remote connection with any volcanic phenomena.

THE NATURE OF SOLUTIONS.

By S. U. PICKERING, M.A.

I BEG to announce that I have this day succeeded in isolating in the solid crystalline form one of the hydrates of sulphuric acid, the existence of which in solutions I had lately predicted from a study of the densities and heat of dissolution of sulphuric acid solutions of different strengths (*Proc. Chem. Soc.*, 1889, 88; and CHEMICAL NEWS, lix., 249). The new hydrate is $H_2SO_4,4H_2O$, containing 57·66 per cent of acid. The proof of its existence depends on its having a definite melting-point at $-25°$, which is lowered (as far as about $-70°$) by the addition of excess of either water or sulphuric acid, and on other evidence which it is not convenient to give in the present place. The isolation of one of the hydrates with either 2, 4, 5, or $9H_2O$ had been rendered probable by a study of the freezing-points of sulphuric acid solutions, and the nature of the curves representing the freezing-points of solutions from which the tetrahydrate crystallises renders it highly improbable that any other hydrate will be obtained in the solid form except, of course, the monohydrate, which has long been known. Such an absolute proof of the conclusions which I have drawn from other sources must place those conclusions beyond doubt, and must establish as an incontestable fact the existence of hydrates in solution.

July 31, 1889.

Carbolic Disinfectants.—We have received from Messrs. F. C. Calvert and Co., of Manchester, a selection of carbolic acid preparations. Their Carbolic Vaporiser is not only useful in sick rooms, but it will be found valuable for driving away gnats and other winged pests. Of similar value against gnats, flies, and mosquitoes is the Carbolic and Camphor (Anti-mosquito) Soap, with which, if a man washes himself liberally, he is supposed to pass freely through the most gnat-haunted district. The Prickly Heat Soap is useful against one of the minor inconveniences of such tropical weather as we have lately passed through, whilst the Dento-Phenolene Mouth Wash will be much appreciated by smokers.

UNIVERSITY COLLEGE, LONDON.
TECHNICAL TRAINING IN CHEMISTRY.

IT is becoming generally recognised that it is necessary, if our manufacturers are to compete on equal footing with continental rivals, to give a more complete scientific and practical training to those about to engage in business or manufactures in which a competent knowledge of chemistry and chemical technology, with its coadjutors, chemical engineering and construction, are required. A discussion at various centres of chemical industry on the training necessary for manufacturing chemists has been published in the June number of the *Journal of the Society of Chemical Industry*, and a unanimous opinion has been elicited that the day is past when a man can enter on any pursuit connected with chemistry without previously equipping himself with a thorough training in chemistry as well as in allied subjects. It is only by aid of such a complete training that the English nation can hope to compete on equal terms with foreign rivals; and without such an education no young man can look forward to engaging in manufacture with any prospect of success. It is especially necessary that firms which are looking forward to enrolling young men as partners, or who intend them to occupy higher official positions, should take steps to give them as complete an education in the necessary subjects as possible. It is an investment which certainly yields the largest possible returns both on outlay and capital.

Mr. Ivan Levinstein, of Manchester, the well-known manufacturer of chemicals and colours, has delivered the following opinion on the industrial value of technical training, under the auspices of the National Association for the Promotion of Technical Training, which he has kindly allowed us to quote:—

"Probably in no branch of chemical industry is technical instruction of greater value than in the coal-tar colour manufacture, with which I am connected, and in no branch has our progress, compared with that of some of our competitors, been more unsatisfactory. For example, the exports of coal-tar products from Germany increased from 195,380 cwts. in 1884, to 319,922 cwts. in 1887, while, as is well known, our exports in these articles have been decreasing. Although this remarkable progress on the part of Germany is, in my opinion, by no means exclusively due to the superior education of their scientific chemists, still the fact is indisputable that greater attention ought to be paid to the training of our young men who desire to enter colour works. Every year a large number of young men issue from our technical schools, who wish to find employment as chemists, the majority of whom are by no means adequately prepared for the purpose. Manufacturers continue to show a preference for German or Swiss chemists, to whom they are often willing to give much higher salaries than to men incompletely trained in our own schools. The whole of the blame of this state of things is not to be laid on our technical schools, especially the best of them; the fault lies to some extent with the parents and advisers of these young men, who, in entire ignorance of what is really required in these days of progress, expect that a youth, having received a mediocre general education and spent two years at a college or technical school, ought at once to be able to earn a livelihood as a chemist in some of our works. We have already far too many of these half-trained chemists. It is not increased quantity but improved quality which we want, and unless this fact is fully recognised, the erection and establishment of new colleges and technical schools will do very little to improve our position.

"The study of chemistry is very laborious and difficult, and no youth should decide to embrace such a career, in any of its departments, unless he has the natural inclination and talent for scientific work, and the means to devote a considerable period of time to the acquisition of

a thorough knowledge of general subjects, as well as of the science to which he intends to give special attention.

"It is clear that the existence of the two first of these requisites can only be ascertained by developing science-teaching throughout our educational system.

"No difference should be made in the general and scientific education of the student, whether he intends eventually to become a teacher or a professional chemist in a manufactory or on his own account; because the ultimate choice will depend largely on circumstance and on individual capacity. It is, in my opinion, a great mistake to believe that a chemist in a manufactory or works requires less knowledge of the science than a teacher or an experimental chemist.

"Now, as regards the arrangements in the teaching institutions which profess to prepare and complete the education of chemists, I would advise that no one should be admitted as a regular or ordinary day student who has not passed a very strict and high-class examination in general subjects. Further, no certificate of efficiency should be given unless the student, after having passed the preliminary examination, has attended, for at least three years, the courses of lectures on chemistry and kindred subjects and the laboratory courses prescribed at one or other of the recognised institutions.

"By this time he will probably have made up his mind as to whether he intends to adopt the career of chemist in works, or that of an experimental or analytical chemist. In either instance he might with advantage continue his course of study for another twelve months, substituting for any subject which had no special bearing on his future work a course, say in chemical engineering and the construction of chemical plant, or, if he intends to seek employment in colour, dye, bleach, or print works, a course in dyeing, printing, and bleaching. It is obvious, however, that it is not sufficient that the youth himself should possess all the qualifications required; his successful training will naturally depend largely on the teaching staff, and it is especially to the selection of teachers of chemistry that very great attention must be devoted. They should not only be capable teachers and distinguished men of science, but should also possess talent and originality, and they should be placed in such a position as to be entirely independent of the necessity of undertaking any work which lies outside their sphere."

Perhaps the most successful school of applied chemistry in existence is that of Prof. Lunge, at the Zürich Polytechnikum. He expresses the following opinion on the necessity of education in chemical technology:—

"In my opinion a young man who aspires to the position of a works' chemist with the view of afterwards becoming practical manager of a chemical factory, should be well educated in a general way to begin with: he should have a thorough grounding in mathematics and in French and German, and, if possible, in the elements of geometrical drawing. When entering upon his proper chemical training he should begin with a purely scientific study of chemistry and physics, not forgetting mathematics, mineralogy, geology, and even biology, and he should be thoroughly taught to practise chemical analysis and to manipulate apparatus of all kinds. Later on he must learn to make even the most difficult of chemical preparations. Only when he has laid a thorough 'scientific' foundation he must begin with technology, chemical as well as mechanical, which in such disciplinary course indeed cannot be kept separate, since in chemical technology he must be made acquainted with the mechanical means of carrying out chemical operations on a large scale. This he should learn well, and he should supplement his class-work by learning to express his technical ideas on the drawing-board."

Dr. Lunge concludes as follows:—"I must conclude by stating my conviction, founded upon thirteen and a half years' teaching experience, preceded by sixteen years' manufacturing practice, that in the long run a man who has combined in his studies a really thorough scientific with an appropriate technological training, will have a great advantage both over the pure theorist and over the mere 'practical man.'"

To meet this want a syllabus of lectures and laboratory instruction has been arranged at University College, a college the chemical traditions of which are adorned by the names of Turner, Thomas Graham, Fownes, Williamson, and Charles Graham, all of whom have had the most prominent influence on the development of scientific and industrial chemistry.

THE ELECTROLYSIS OF DISTILLED WATER.

By M. E. DUTER.

THE author has employed in his researches distilled water contained in glass tubes with two limbs, which, even after the lapse of several months, did not communicate any alkalinity to the water. The electromotive power employed was considerable, always about 100 volts.

As electrodes were used: (1) an anode and a cathode of platinum; (2) anodes formed of very different metals, chiefly nickel, cobalt, iron, or copper, the cathode being still platinum; (3) an anode of platinum with a cathode of tin, of bismuth, of copper, of lead, of mercury, or of aluminium. In the first case, if the cathode is a fine wire whilst the anode is a broad plate, electrolysis yields for several days nothing but hydrogen. Afterwards oxygen begins to appear at the positive pole, but its volume is always less than half the volume of the hydrogen liberated. Water thus submitted to electrolysis acquires a slightly acid reaction. In the second case the anodes are attacked, and during the first hours of the action they yield monoxides. At the positive pole there appears a jelly which is green with nickel, rose with cobalt, and blue with copper. After some hours the oxides take a darker colour and pass into peroxides. If the electrolysis is let continue for some months the oxide surrounding the positive pole is finally partially reduced. Thus nickelic oxide returned to the nickelous state and became green; cobaltic oxide, which was maroon, became a rose, and that of iron lost its rusty colour and turned almost white. This transformation requires about two months; for ferric oxide it only begins after seven or eight months. It seems as if these deoxidations may be compared with those produced in hydrogen peroxide by oxygenated water. In the third case, where the negative electrode is constituted of a metal other than platinum, this metal, contrary to expectation, is generally oxidised. Tin yields stannic oxide with escape of hydrogen. Bismuth yields similar results. A negative electrode of copper is covered with a deposit which almost stops the passage of the current, even with an electromotive power of 120 volts. Lead at the negative pole is covered with grey tufts, which, if the current is interrupted, give rise to a plumbous oxide, which seems to flow from the electrode like a thin white paste. If the negative electrode is of mercury the free surface of the metal covers itself with asperities of a pasty aspect, which liberate hydrogen and continue so to do for more than an hour after the cessation of the current.

Aluminium is energetically attacked at the negative pole, becoming transformed into alumina. After a time the metal loses its cohesion, splits up, and falls to the bottom of the vessel in the form of fine laminæ and of grey powder.

These experiments, and especially that with aluminium, render it probable that metallic hydrides are formed at the negative pole and are then destroyed by the water with formation of oxide and escape of hydrogen.—*Comptes Rendus* (cix., p. 108).

ON PRECIOUS STONES.*

By GEORGE F. KUNZ.

Gem Mining.—During 1887 no work was done either at Mount Mica, Paris, Maine, or at Stony Point, North Carolina, which are the two most noted localities where gems are sought for systematically. At Mount Apatite, Auburn, Maine, some work was carried on during the fall of 1887; 200 dollars worth of tourmalines and 400 dollars worth of other minerals were found.

Several localities in North and South Carolina and Kentucky have been opened and ordinary mining operations carried on for the purpose of producing zircon, and several other comparatively rare minerals which have been only looked upon as gems as heretofore, but are now used for making the oxides of zirconium, lanthanum, cerium, &c. These oxides are needed for manufacturing purposes.

Exceptional Discoveries of Gems—Diamond.—In April, 1887, Mr. Lewis M. Parker, a tenant on the farm of Daniel Light, three-fourths of a mile north-west of Morrow Station, and thirteen miles south of Atlanta, Georgia, found a diamond on the farm. The stone afterwards came into the possession of Mr. W. W. Scott, of Atlanta, who sent it to the writer for examination. It proved to be an octahedral crystal weighing $4\frac{1}{16}$ carats (828 m.grms.), two-fifths of an inch long and one-fourth of an inch wide. It measured 9 by 10 by 7 m.m., is slightly yellow, and has one small black inclusion. The specific gravity was found to be 3·527. Curious long shallow pittings mark the surface. A stone of from $1\frac{1}{16}$ to 2 carats could be cut from it.

Mr. L. O. Stevens, of Atlanta, Georgia, has informed the writer that a coloured man called on him during the past year with a 2-carat diamond, defective and of poor colour, which he stated he had found in his garden within a few miles of Atlanta. He has shown no desire to sell or lend the stone for examination.

Zircon.—Opaque green zircons in crystals 1 inch long and 1¼ inches wide, were found by Mr. Nimms in Saint Lawrence county, New York, at the town of Fine. They were curious, but not of gem value. Fully 25 tons of this mineral will be raised during 1888, from Henderson county, Kentucky, for use in a new incandescent gas-burner manufactured in Philadelphia.

Beryl.—Prof. Eugene A. Smith obtained from Coosa county, Alabama, some light golden yellow beryl of sufficient transparency to furnish small gems. Blue-green beryl that afforded fair gems was reported by Mr. William E. Hidden, from Mitchell county, near the Yancey county line, North Carolina.

Phenacite.—Dr. S. L. Penfield describes phenacite from Topaz Butte, 5 miles north of Florrissant and the same distance from Mount Antero, Colorado. Mr. W. B. Smith describes the occurrence of topaz and phenacite at Topaz Butte (*American Journal of Science*, February, 1887, III. Series, vol. xxxiv., p. 130). An extensive find of phenacite crystals (few of gem value, however,) associated with aquamarine crystals, was made at Mount Antero, Colorado, in the fall of 1887. The phenacites were almost quartzoids in form. The occurrence is described by the Rev. R. F. Cross, in a note in the *American Journal of Science*, February, 1887, p. 161, vol. xxxiv.

Garnet.—A variety of spessartite garnet was found at Amelia Court House, Virginia, in masses several inches across, and dark brown, dark red, or honey-brown in colour, which would afford cut gems from 1 to 10 carats in weight. These are the finest specimens of this variety of garnet yet found. Fully 1½ tons of the almandite garnets of Salida, Colorado, were found during the past year and sold as tourists' or mineralogical specimens at from 30 cents to 1 dollar a pound. One absolutely perfect dodecahedron weighed over 14 pounds. In the *Proceedings of the Philadelphia Academy of Natural Sciences*, 1886, p. 355, Dr. George Koenig describes a titaniferous garnet from south-western Colorado, and also analysis of schorlomite from Magnet Cove, Arkansas, which he finds to be titaniferous garnet.

Tourmaline.—A large number of green tourmalines, some quite stout and several inches in length, have been found at Franklin Furnace, Sussex county, New Jersey, but although they are an important addition to our mineralogical collections, and the outer parts of some of the crystals are of a rich almost chrome green, yet not a single one was observed which would cut a transparent gem of even a few carats.

Prof. R. B. Riggs, of the laboratory of the Geological Survey, recently made over 25 analyses of tourmalines of all colours. He found the question of the colour of the lithia tourmaline a very interesting one. The colour of the iron and magnesian varieties depends on the amount of iron present. It ranges from the colourless De Kalb through all the shades of brown to the Pierrepoint black, whilst the lithia tourmaline, containing more or less manganese, gives the red, green, and blue, as well as the colourless varieties. The shades of colour do not depend on the absolute amount of manganese present, but rather on the ratios existing between that element and iron. Thus, when the amount of manganese bears a specific proportion to the iron, we have the colourless pink or very pale green tourmaline. An excess of manganese produces the red varieties; and if the iron is in excess the various shades of green and blue result.

Rubellite.—Mr. William Irelan, jun., reports the finding of transparent rubellite in fine crystals 1 to 2 inches long, in San Diego county, California.

Hiddenite.—Rev. Alfred Free, in a report on a placer mine at Bracket Town, McDowell County, North Carolina, mentions the finding of a small crystal of spodumene of the hiddenite variety. He had also observed blue, green, and pink tourmaline at the same locality.

Rock Crystal.—In the last report reference was made to the occurrence of rock crystal in what was believed to be a part of Virginia, but which, on visiting the locality, the writer found was merely the mountainous part of Ashe county, North Carolina. My attention was first called to this locality by the receipt thence, by Messrs. Tiffany and Co., of a 51-pound fragment of a large crystal, which was said to have been broken from a mass weighing 300 pounds by a twelve-year old mountain girl. This large crystal was found on the Mintor Blevin Farm, on Long Shoal Creek, in Chestnut Hill township, though crystals have also been found at two places 600 feet apart on the L. C. Gentry farm, about one mile from the former locality. All three places are 50 miles from Abingdon, Virginia, and 40 miles from Marion, Virginia. Crystals have also been found close to the north fork of Piny Creek, on the Saint Ledger Brooks Farm. At the latter place was found a remarkably clear distorted crystal, weighing 20½ pounds, which is absolutely perfect, and is the finest piece of rock crystal ever found in the United States; and on the Gentry Farm one crystal was found weighing 188 pounds and another weighing 285 pounds. The latter was 29 inches long, 18 inches wide, and 13 inches thick, showing one pyramidal termination entirely perfect and another partly so; it sold for over 500 dollars for use in the arts. A number of others have also been found. All these localities are on a spur of Phœnix Mountain, and the crystals have all been found in decomposed crystalline rocks, principally coarse felspathic granite, which has all decomposed, even to a greater depth than that at which these crystals occur. Most of them are obtained by digging where one crystal has been found, or by striking and unearthing them with a plough. Altogether several dozen crystals have been found, weighing from 20 to 300 pounds each, and future working will doubtless bring many fine ones to light. Some of these afford larger masses of clear rock crystal

* Abstract from "Mineral Resources of the United States."

than have ever before been found in the United States, and suggest its use for such objects of luxury as crystal balls, clock cases, mirrors, &c., which are now to be seen in the Austrian treasury at Vienna.

From the vicinity of Fairfax county, Virginia, Mr. James W. Beath obtained quartz with alternate green and white veinings, the green being produced by chloritic inclusions. When cut it forms an interesting ornamental stone, and several hundred dollars' worth of it have been sold.

Mr. H. L. Hosmer reports that crystals of smoky quartz a foot in length are occasionally found at Sterling, Montana.

Chrysoprase.—Mr. William Irelan, jun., reports from Tulare county, California, beautiful semi-transparent chrysoprase of fine colour. This has also been found in Douglas county, Oregon.

Agate.—At Sioux Falls, Dakota, the company that is cutting and polishing the agatised wood from Arizona and the quartzite found at Sioux Falls has, after a great deal of experimenting, perfected the methods of sawing and polishing hard materials so as greatly to reduce the cost. Among the objects produced were a round column 11¼ inches wide and 21 inches high, cut transversely across the tree so that the heart was visible on two sides of it, with the radiations in all directions; and sections measuring 25, 24, 17½, and 13 inches in diameter, respectively, so highly polished that when turned with the back to the light they form a perfect mirror. All the specimens were brilliant in colour and rivalled any work ever done in hard materials. The company has removed from the forest 180 tons of material, and 20 tons of sections have been ground down to show its characteristic beauties. Perhaps 100,000 dollars worth is now undergoing the cutting and polishing process.

Pectolite.—A massive pectolite of unusually dense structure has been announced by Mr. William P. Blake as occurring in Tehama county, California, in masses of considerable size and susceptible of a high polish. In a letter to the writer he gives the following description:—"It occurs in a vein, and is broken out in rough tabular masses from 2 to 3 or more inches in thickness, but it is reported that much larger masses can be obtained. It is exceedingly tough and hard to break. The punctured surfaces are irregular, without cleavage, but have a silky lustre and crypto-crystalline structure, exhibited in extremely fine inseparable fibres, which are radial, curved, and interlaced, and are perhaps embedded in a siliceous magma, but the fibres constitute the bulk of the mass. the colour is white, with a delicate shade of sea green, and translucent. Exposed or weathered portions lose their-porcelain like translucency, and become white and somewhat earthy in appearance, and exhibit the crypto-fibrous structure with more distinctness. Specimens cut and polished across the end of a slab-like mass show on one side a narrow selvage of breccia, made up of fragments of the pectolite and of dark coloured wall rock mixed and firmly cemented together. On the opposite side or border of the mass there are distinctly formed parallel planes of concentric layering, from the surfaces of which the fibres diverge. These layers and the brecciated border opposite show the vein-like formation of the mass between the walls. The hardness is 6 to 6·5. In the blowpipe flame it burns to a white enamel and gives off a little water. It may be found useful as an ornamental stone for making small objects—cups, plates, handles, or for carving figures, or inlaid work." This is identical with the pectolite from Alaska, described by Prof. F. W. Clarke.

Peristerite.—Large quantities of peristerite are reported by Mr. C. M. Skinner at Cavendish, Vermont, near Cavendish Falls, in the railroad cut, 22 miles north-west of Bellows Falls.

Oligoclase.—Of great interest is the transparent oily green oligoclase containing small, white, star-like inclusions, which impart to the mass all the appearance of green glass, and with included white minerals found at a depth of 400 feet in mica near Bakersville, North Carolina. It was found by Mr. Daniel Bowman.

A very interesting variety of sunstone was found by Mr. J. A. D. Stephenson at the quarry in Statesville, North Carolina. Several hundred dollars' worth of it has been sold as gems.

Albite.—In the Allen mica mines at Amelia Court House, Amelia county, Virginia, as a by-product in mica mining, a remarkable series of albite has been found, tabular, but measuring 4 to 7 inches in length and forming large groups; also the same mineral in massive form of the moonstone variety, and tons of amazonstone in bright cleavages.

Rhodonite of the variety known as fowlerite has been found in Franklin Furnace, New Jersey, in groups of rich, flesh-coloured crystals finer than ever before known. Some of these were 6 or 7 inches in length and several inches thick, forming groups a foot across. Although of value for gem material, they possess a higher mineralogical value, and more than 1000 dollars' worth was sold for specimens. The rhodonite so well known as occurring in boulders at Cunningham, Massachusetts, has recently been traced to the ledge, and we may now hope to see this stone used extensively for decorative and ornamental purposes, as at this locality it is one of the richest pink and flesh-coloured minerals known.

Turquois.—Additional evidence of the antiquity of the turquois workings of New Mexico and Arizona has been gathered by the Hemenway expedition, sent out by Mrs. Hemenway under the direction of Mr. Frank H. Cushing. About ten miles from Tempe, Arizona, where the excavations are being made, a shell encrusted with turquois and garnet representing the form of a frog was found.

Cyanite.—Mr. Daniel A. Bowman communicates that the cyanite mentioned in the last report was found near the summit of Yellow mountain, alongside the road to Marion, about 4 miles south-east of Bakersville, North Carolina, at an altitude of 5500 feet. Some of this is transparent, from one-eighth to one-half inch across, and several inches long. So rich is its colour that it was sold for sapphire. Its low hardness unfits it to some extent for use as the gem for which it is to be worn. It is a handsome mineralogical gem, however.

Crocidolite.—In the *American Journal of Science*, III., vol. xxxiv., p. 108, Prof. A. A. Chester published analyses of the crocidolite from Beacon Hill Pole, Cumberland, Rhode Island, an interesting occurrence of this mineral, though not in gem form.

Labradorite.—The well-known Labradorite rock in Lewis county, New York, is so plentiful that the reflection of the boulders has given the river that runs through the locality the name of Opalescent River. This is being extensively cut as an ornamental stone.

Mexican Onyx.—The handsomest and lowest priced of our ornamental stones, and one which has been introduced most extensively, is the so-called Mexican onyx or Tecalli, as it was first called, from the town of that name in the state of Pueblo, Mexico, where it is found. The deep colours are richer than those of any marble known, and its wavy stalagmitic structure and the high polish which it can take have made it popular throughout the whole civilised world. With a metal mounting the effect is greatly enhanced. It occurs in almost unlimited quantities, and fully 500,000 dollars worth has been used in the United States for table tops, mantels, vases, &c.

(To be continued).

Occurrence of Ferrous Oxide in Potassium Sulphocyanide.—J. Kranzfeld (*Pharm. Zeitung für Russland*).—Such sulphocyanide turns red on exposure to air, and is of no use for the detection of iron. It may easily be purified by solution in aqueous alcohol, addition of a ew drops of ammonium sulphide, and filtration.

NOTICES OF BOOKS.

Scientific and Industrial History of Aniline Black (Histoire Scientifique et Industrielle du Noir d'Aniline). By E. Noelting, Director of the School of Chemistry, at Mulhouse. Mulhouse: Strickelberger.

This work opens with a very elaborate history of aniline black, in which the name of Lightfoot is not once mentioned. We find accounts of experiments and observations made both in the laboratory and in industrial establishments, some before and some subsequent to Lightfoot's invention. But the former led to no definite and tangible results, and the latter, save the discovery of the remarkable action of the vanadium salts, have been more curious than useful.

In the second chapter the industrial applications are brought forward. After speaking of the use of aniline blacks in powder, the author passes to the formation of blacks upon the fibre. Here, at last, we find a notice of Lightfoot. It is said that he "introduced into the production of aniline black an improvement such that he is generally considered as its originator"—a view which M. Noelting by no means seems to share. But the real motive of the book is made to appear in the preface. The author writes:—"In many countries the application of aniline black is entirely free; in France the patents of M. Grawitz claim the monopoly of this industry, and have led to much litigation. It seems to us important to submit the patents of M. Grawitz to a thorough discussion."

This, of course, is a very delicate matter. We are not sure how far the discussion, even of foreign patents, with reference to their validity, is safe in England. Hence, pending the necessary restriction of English libel law, we shall not express any opinion on the matter at issue.

CORRESPONDENCE.

THIOCAMF.

To the Editor of the Chemical News.

Sir,—In Chem. News, vol. lx., p. 36, I noticed a letter from your correspondent, Thos. T. P. Warren, on thiocamf, now being used as a disinfectant, and stating that the preparation, a solution of camphor in sulphurous acid, was the invention of Alexander Parkes, and patented by him, No. 11,147, 1846, as a solvent of indiarubber.

As the inventor of the cold converting process of vulcanisation, I wish to say that, although in my specification nothing was said of this peculiar property of the camphor solution, I was well aware of the fact, as both camphor and sulphurous acid separately are disinfectants, and a friend of mine wished to join me in bringing it out for this purpose. Being, however, much engaged at that time with other important matters, I could not go into it, and it passed from my memory. Still the original idea was my own, and my only object in troubling you with this letter is to point this out to your readers.—I am, &c.,

Alexr. Parkes.

Chancellor Rd., Dulwich,
August 1, 1889.

Detection of Jute in Linen or Hempen Tissues.—The warp, which generally contains the jute, is freed from the weft and dipped in the solution of an aniline salt. Linen and hemp remain unchanged, whilst raw jute is stained an intense yellow. To test for bleached jute the thread is plunged into a solution of chloride of lime, drawn out, taken through hydrochloric acid, washed, and touched with ammonia. The presence of jute is shown by a characteristic violet-red colour, whilst linen and hemp turn brown.—*L'Industrie Textile* and *Chemiker Zeitung*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 4, July 22, 1889.

On Zinc and Cadmium Chromites.—G. Viard.—The author obtains these compounds by a modification of Gerber's process. He causes the vapours of the chlorides, carried along by a slow current of nitrogen or carbon dioxide, to act upon neutral potassium chromate. Both the chromate and the chloride are placed in boats in a porcelain tube. The zinc chromite forms black regular octahedral crystals, hard enough to scratch quartz and not attacked by acids. The cadmium compound is formed by a similar process, and yields crystals which scratch glass, but not quartz.

Formation of Crystalline, Alkaline, and Alkaline-Earthy Platinates at High Temperatures.—G. Rousseau.—The author has observed the rapid corrosion of platinum crucibles by basic fluxes. The products obtained were often mixed with metallic platinum; sometimes, also, when the fluxes were very alkaline, the crystals collected contained considerable quantities of platinic oxide united to cobalt, iron, and aluminium oxides. This unexpected formation of alkaline and alkaline-earthy platinates was observed between 800° and 1300°. The author has studied the barium and sodium platinates, which represent two very distinct types. In stability the platinates are comparable to the manganites and the ferrites. They present a new instance of the formation of a compound at temperatures higher than the point of their decomposition.

On the Ammonio-cobaltic Tungstates and Vanadates.—Ad. Carnot.—This paper will be inserted in full.

On Diethyl-amido-α-propionic Acid.—E. Duvillier.—This compound is obtained at a temperature of 100° by the reaction of 1 mol. of α-bromo-propionic acid upon about 3 mols. of aqueous diethylamine. The acid is very soluble in alcohol and in water, which it attracts as eagerly as does calcium chloride.

The Application of the Measure of Rotatory Power to the Study of the Compounds Resulting from the Action of Malic Acid and Ammonium Molybdate.—D. Gernez.—The progressive addition of ammonium molybdate to a solution of malic acid determines an increase of rotation, the initial value of which, 0·12, gradually reaches a maximum value of −5·19, or 35 times the rotation of the malic acid contained in the solution. This maximum corresponds to a combination of 9 equivs. of malic acid to 1 of ammonium molybdate. As this salt contains 3 equivs. of ammonia, the compound contains 3 equivs. of base to 1 of acid. For weights of the molybdate greater than one-ninth of the equivalent the rotation retrogrades, passing from left to right, and augments progressively. An abrupt variation in this increase sets in when the liquid contains 3 equivs. of acid to 1 of the salt. An attentive examination of the progress of the phenomena shows that at the outset very slight quantities of the molybdate produce considerable effects; thus, 1-384th equivalent of ammonium molybdate doubles the rotation presented by the active liquid.

Detection and Determination of Sodium Hydrocarbonate in Milk.—L. Padé.—This paper will be inserted in full.

Improvements Introduced in the Preparation of Crystalline Hæmoglobine by Hoppe-Seyler's Process: New Method for Preparing this Body.—M. Mayet.—This memoir will be inserted at some length, if possible.

Moniteur Scientifique, Quesneville.
4th Series, Vol. iii., May, 1889.

On the Theory of Dyeing and on the Causes of the Spots Observed on Dyeing Cloth.—Dr. Paul Julius.—Among the products of the decomposition of wool under the influence of water, alkalies, and acids there are compounds soluble in water and others which are insoluble, and which are able to precipitate many colours and mordants from their solutions in the form of insoluble lakes. The inequalities often observed in dyeing woollen cloth are due to the presence of such products.

Formation of Saccharic Acid as a Characteristic Reaction of Dextrose.—R. Gans and B. Tollens.—From *Liebig's Annalen*.

A Novel Alkaloid: "Imperialine."—M. Fragner (*Berichte*).—This alkaloid, $C_{35}H_{60}NO_4$, is obtained from the bulbs of the fritillary. Its characteristic reactions are:—Strong sulphuric acid turns imperialine a pale yellow; if ground up with sugar and moistened with sulphuric acid it turns first a yellowish green, then a light brown, a flesh colour, a cherry-red, and lastly a dark dirty violet. With Tröhde's reagent it takes a light yellowish green; with Mandelin's reagent an olive green, then a reddish brown, and lastly a dark brown.

Manufacture and Purification of Carbon Disulphide.—Ignatius Singer.—From the *Journal of the Society of Chemical Society*.

On Yorkshire Grease.—G. H. Hurst.—From the *Journal of the Society of Chemical Industry*.

Rapid Analysis of Prussian Greens.—A. Chenevier.—Prussian green is a pigment much used in paint and varnish. It is a mixture of chrome yellow and prussian blue let down with lead and calcium sulphates, ochre, china clay, &c. The colour is ground up in water acidulated with hydrochloric acid and placed in a stoppered flask. Potassium iodide is added in slight excess. It is digested, starch paste is added, and it is titrated with decinormal sodium thiosulphate. In presence of prussian blue it is impossible to catch the end of the operation. Therefore, for a speedy and approximate determination after the addition of each c.c. of the thiosulphate, a drop of the liquid is placed upon a plate of copper. As long as this liquid contains free iodine it leaves upon the plate a white spot of copper iodide. As soon as the thiosulphate is in excess no spot is produced. If more time is available the following modification of the process may be used:—2·16 grms. of the green well ground up in a glass mortar with a little water and 2 to 3 c.c. of hydrochloric acid (sp. gr., 1·18) are placed in a graduated and stoppered jar of 200 c.c.; 3 to 4 grms. of potassium iodide are added and the whole is let digest for fifteen minutes. The jar is filled up to 200 c.c. with water, mixed, and let let settle for two hours. At the end of this time 100 c.c. of the clear liquid, corresponding to 1·08 of the green, are drawn off with a syphon. In this liquid the free iodine is determined with decinormal thiosulphate, using starch-paste as indicator. Each c.c. represents 1 per cent of lead chromate. The process is accurate to 0·2 or 0·3 per cent. *Determination of the Prussian Blue.*—To 4 grms. of the green ground up with 10 c.c. of water and 5 c.c. of hydrochloric acid are added 3 to 4 grms. of ferrous sulphate dissolved in 20 c.c. of water to reduce the lead chromate. After digesting from five to ten minutes an excess of soda-lye is carefully added, which precipitates the oxides of iron and decomposes the blue. It is poured into a flask marked at 200 c.c. and heated almost to a boil. When cold the volume is made up to 200 c.c. After settling, 100 c.c. of the clear liquid (corresponding to 2 grms. of the green) are drawn off, and, after acidulation with sulphuric acid, titrated with permanganate.

Method for Removing Nitrogen Compounds from the Sulphuric Acid used in Kjeldahl's Process.—G. Lunge (*Zeits. f. Angewandte Chemie*).—The author criticises the method of Meldola and Moritz, who propose to add a small quantity of sodium nitrite and heat strongly.

Determination of Nitrogen. Methods Officially Adopted by the Congress of American Agricultural Chemists.—Already noticed.

Determination of Phosphoric Acid Adopted as Above.—Already noticed.

New Methods of the Elementary Analysis of Organic Substances in the Moist Way.—J. Messinger (*Berichte* and *Chemiker Zeitung*).—The author finds that all organic substances, if heated in an undiluted sulphuric solution with chromic acid, undergo a complete combustion. The carbon is liberated as carbon dioxide; nitrogen escapes as such, or as ammonia. The sulphur, phosphorus, and arsenic remain as sulphuric, phosphoric, aud arsenic acid. The halogens are set at liberty.

Convenient Method for Preparing Oxygen.—C. F. Gœhring (*Chemiker Zeitung*).—The author uses oxygenated water as material.

Determination of Paraffin.—B. Pawlewski and J. Filemonowicz.—Already noticed.

Employment of Diazo-compounds for Detecting Organic Substances in Water.—P. Griess (*Berichte*).—Already noticed.

Composition of Gums and Resins.—Williams.—From the Chemical News and *Chemiker Zeitung*.

Determination of the Higher Alcohols, especially of Amylic Alcohol, in Brandies and Industrial Alcohols (*Chemische Industrie*).—Already noticed.

On Dextro-rotatory Honey.—Dr. E. O. von Lippmann.—The author notices the presence of saccharose in honeys obtained from hives situate near sugar refineries. Such honey is deficient in aroma.

Assay of Peppers.—J. N. Zeitler (*Zeitschrift f. Angewandte Chemie*).—Already noticed.

Artificial Coffee.—A notice of fraudulent coffee beans moulded in a machine, for which a patent has been actually granted in Germany.

Historical Account of the Development of the Textile Industry.—Dr. O. N. Witt.—A translation of an entire work and not admitting of useful abstraction.

The Favier Explosives.—A reply to a memoir of German origin, unfavourable to the Favier explosive.

Industrial Review and Patents.—Abridged specifications of a number of chemical patents, chiefly of German origin.

Volumetric Determination of Stannous Compounds.—Adolf Jolles (*Chemiker Zeitung*).—The author adds to a known volume of a solution of alkaline manganate of known strength the solution of stannous salt to be determined, with frequent agitation until the green colour passes into a yellowish brown. The solution of manganate is made by dissolving in a beaker 4 to 5 grms. potassium manganate and 8 to 10 grms. potassium hydroxide in water, transferring the clear solution cautiously into a litre flask and filling up to the mark. For standardising, exactly 5 or 10 c.c. of the manganate solution are run into an Erlenmeyer flask and a solution of tartar-emetic (10 grms. of the pure salt per litre) is added, with frequent agitation, until the green colour turns to a yellowish brown. For standardising the stannous salts from 0·2 to 0·4 grm. of the salt in question, or of tin, is dissolved in hydrochloric acid in a current of carbonic acid; the clear solution thus obtained is poured into a 250 c.c. flask and filled up to the mark. Exactly 5 or 10 c.c. of the standardised manganate solution are dropped from a burette into a small Erlenmeyer flask and the stannous chloride solution is added, likewise from a burette, with frequent agitation, untill the yellowish brown colour appears.

MISCELLANEOUS.

Cooking by Electricity.—The Hotel Bernina, at Samaden, has for some time been lighted with electricity, power being supplied by a waterfall. As during the day this power is not required for lighting, and is therefore running to waste, the proprietor of the hotel has hit upon the idea of utilising the current for cooking when it is not required for lighting, and an experimental cooking apparatus has been constructed. This contains German silver resistance coils, which are brought to a red heat by the current, and it has been found possible to perform all the ordinary cooking operations in a range fitted with a series of such coils.—*Engineering and Mining Journal.*

Remarks on the Physiology of Tannin. — F. Reinitzer.—The author protests against the present universal custom of giving the name "tannin" or "tannic acid" to all vegetable compounds which give with ferric chloride blue or green colourations or precipitates, and which are precipitated by solution of gelatin. As regards the former reaction he points out that ferric chloride colours aqueous solutions of mono- or polyvalent phenols blue, green, or violet. Hence he considers it very probable that the tannins contain hydroxyl-groups with a phenolic character. He further reminds us that many tannins do not precipitate solutions of gelatin at all, others occasion merely a turbidity, and others again produce a very imperfect precipitation. He doubts whether all these bodies can fulfil the same physiological function, and considers the idea of "tannin" about equal in value to that of "bitter principle," under which substances of very different character were formerly included. — *Deutsch. Botan. Berichte* and *Chemiker Zeitung.*

Poisoning by Cotton Dyed with Lead Chromate.—Th. Weyl.—Dr. Carry, of Lyon, reports on a series of poisoning cases among women engaged in winding yellow or orange yarns. All the symptoms indicated lead-poisoning. Prof. Pouchot, of Lyon, however, found in three samples submitted to his examination no lead, and stated that the yarns were mordanted with a salt of antimony and dyed —No. 1 with Martius' yellow, No. 2 with Jaune solide, and No. 3 with "Jaune N Poirrier." The writer obtained, at the request of Dr. Carry, specimens of the suspected yarns, and found, in concert with G. Schulz, of Berlin, that they were dyed with lead chromate, and not with the dyes above mentioned. Both the lead and the chrome were not merely qualitatively recognised, but quantitatively determined. How Prof. Pouchot can have been deceived is questionable. The use of lead chromate is legal both in France and Germany. In an appendix the author mentions that he found in a saddler's workshop in Berlin sewing thread dyed orange with lead chromate. It could scarcely be doubted that lead poisoning might ensue from the continued use of such thread.—*Zeit. f. Hygiene* and *Chemiker Zeitung.*

Determination of Nitrogen and of Phosphoric Acid in Organic Bodies.—Dr. Otto Lange (*Chemiker Zeitung*).—The author finds that the liquid obtained by the sulphuric treatment of the sample in Kjeldahl's process may be employed in determining the total phosphoric acid. He uses for the attack a flask of 300 to 350 c.c. capacity. He treats 10 grms. of the substance with 50 c.c. of undiluted sulphuric acid and 0·5 grm. of mercury or 0·5 to 1 grm. of copper sulphate. The liquid, after the action is over, is diluted with water to 500 c.c. and an aliquot part is used for the determination of the ammonia formed. Another portion, say 50 c.c. (corresponding to 1 grm. of the substance), is treated with 100 c.c. of Maercker's liquor and 25 c.c. of magnesia mixture. The whole is stirred until the appearance of the precipitate, which may be filtered after fifteen minutes. Maercker employs citric acid 1½ kilos., water 3 litres, ammonia at 24 per cent 5 litres, and adds 7 litres more water.

Modification in the Process of Organic Analysis by Combustion.—W. L. Dudley (*Berichte* and *Chemiker Zeitung*).—The author effects the combustion in a platinum tube of 48½ c.m. in length and 1½ c.m. in diameter, extended at one end by a tube of the same material 13 c.m. in length and ½ c.m. in diameter. The other extremity, serving for the introduction of the substance and the entrance of the gases—air, oxygen, or nitrogen, as the case may be,—is closed by a screw stopper traversed by a tube ½ c.m. in diameter. The arrangement and the progress of the analysis are those usual in combustions with a fixed tube. Behind the boat containing the substance the author places a coil of fine platinum wire gauze, which is easily removed when it is necessary to insert or withdraw the boat. This coil occupies 3½ c.m. in length and serves to burn the vapours.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that JULIUS MARX, of Ulm a/Donau, Wurtemburg, in the Empire of Germany, has applied for leave to amend the Specification of Letters Patent No. 2367 of 1888 for "Improvements in the method of and means for separating matters in solution by osmose, dialysis or diffusion, or by electrolysis, or by a combinaton of those processes."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 31st July, 1889.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed),
H. READER LACK,
Comptroller-General.

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NOTES ON THE ABSORPTION-SPECTRA OF OXYGEN AND SOME OF ITS COMPOUNDS.*

By G. D. LIVEING, M.A., F.R.S., Professor of Chemistry, and J. DEWAR, M.A., F.R.S., Jacksonian Professor, University of Cambridge.

THE absorption-spectrum of oxygen has engaged attention not only on account of the important part which that element plays in the world, but because of the remarkable character of that absorption, so strongly marked, exhibiting bands of two essentially different classes, and extremely variable under varying circumstances of condensation and combination.

It may be expected that the study of it will reveal something new as to the nature of the molecular changes brought about by different circumstances, physical and chemical.

We have already published notes of some of our experiments on this subject (*Phil. Mag.*, September, 1888), and these confirm generally the observations of Egoroff, Janssen, and Olszewski.

A diagram accompanying the paper represents the absorption of 18 metres of ordinary oxygen gas at a pressure of about 97 atmospheres, that is, of a mass of oxygen rather greater than is contained in a vertical column of equal section of the earth's atmosphere. Under the circumstances of the experiment the absorptions A and B are very black, and the lines of which they are composed appear much broader than in the ordinary solar spectrum. The other bands are all diffuse at their edges, and, so far as we have observed, unresolvable into lines. It will be noted that the complete absorption of the ultra-violet rays does not extend quite so far down as the limit of the solar spectrum, though it approaches that limit. There is a diffuse edge of gradually diminishing absorption succeeding the complete absorption, and this fact, together with the rapid diminution of the extent of the complete absorption with decrease of pressure, lead us to class this absorption of the extreme rays with the diffuse bands, which, according to Janssen, increase in intensity as the square of the density of the gas. If that be so, it is unlikely that the limit of the solar spectrum is due to the absorption of ordinary oxygen. For though we may suppose interplanetary space to be pervaded by materials similar to our atmosphere, yet they must be in such a state of tenuity that, although they may to some extent reinforce A and B, they will not add sensibly to the strength of the diffuse bands. Moreover, these bands, though identical in position, so far as the blue and less refrangible part of the spectrum is concerned, with bands observed by Brewster and others in the solar spectrum, are seen much more strongly through our tubes of compressed oxygen than they appear in the solar spectrum with a low sun. The ultra-violet bands, of which the one near N appears in our photographs nearly as strong as the band just above F, and that in the indigo, have not, so far as we are aware, been noticed in the solar spectrum. Probably they would appear if photographs were taken with small dispersion when the sun was low.

As the pressure in the tube diminished, the bands rapidly faded; that in the indigo, with an oscillation-frequency or wave-number about 2240, was the first to disappear, then those near L and O and that near E. At the same time the limit of the transmitted ultra-violet light advanced from an oscillation-frequency of about 3575 at 97 atmospheres, to 3710 at 50 atmospheres, and 3848 at 23 atmospheres. At 20 atmospheres the three bands above C, D, and F, respectively, were still visible, though faint. B remained visible until the pressure was reduced to 2 atmospheres, and A could still be seen, but with difficulty, when the pressure of the 18 metres of oxygen was reduced to 1 atmosphere.

When atmospheric air was substituted for oxygen we found that 7 atmospheres was the limit of pressure at which we could certainly distinguish A, and 18 atmospheres the limit at which we could see B. It is a difficult matter to say exactly when an absorption becomes invisible, but the observations on air were made under the same circumstances as those on oxygen, and the two sets of observations were fairly comparable. With air at 75 atmospheres the three bands above C, D, and F, respectively, could all be seen, but that near C only with difficulty. The mass of oxygen and its *partial* pressure in the tube was in this case less by about one quarter than that which was required to bring out the bands when oxygen alone was used. The cause of this may be that the development of the diffuse bands depends in some degree on the total pressure of the air, and not only on the partial pressure of the oxygen in it.

The mass of oxygen which when unmixed with nitrogen made A visible would correspond to that in the tube filled with air at 5 atmospheres, and that which made B visible would correspond to air at 10 atmospheres. The differences between these pressures and those which are actually needed to render A and B visible seem too great to be ascribed to errors of observation, and seem to indicate that the addition of the nitrogen has some effect on the absorptive action of the oxygen. On the other hand, Egoroff found that he could still distinguish A when the thickness of air at ordinary pressure was reduced to 80 metres (*Compt. Rend.*, vol. ci., p. 1144). This amount of air corresponds to rather less oxygen than our tube would hold at a pressure of 1 atmosphere. Differences in the sources of light, in the spectroscope, and the observers, would, however, count for a good deal in observations of this kind.

In order to try the influence of temperature on the absorption, the shorter of our experimental tubes, 165 c.m. long, was surrounded by a jacket filled with a mixture of solid carbonic anhydride and ether, which was rapidly evaporated by means of a large air-pump. By this means the temperature would be reduced to $-100°$. The absorption of oxygen at several different pressures up to 104 atmospheres was observed through the cooled tube. We were not, however, able to detect any increase of intensity or other change in the absorptions which could be ascribed to the cooling. To try the effect of an increase of temperature the 18-metre tube was surrounded by a jacket and heated up to 100° by steam. Heating appeared to render the diffuse bands rather more diffuse and less distinct. On the whole the influence of a change of temperature of 100° either way is slight.

We have observed repeatedly the absorption of liquid oxygen in thicknesses of 8 and 12 m.m. Our observations confirm those of Olszewski. 8 m.m. of liquid oxygen gives plainly the three diffuse bands above C, D, and F, respectively. With a thickness of 12 m.m. we were not able to detect any more.

We observed the absorption produced by liquid oxygen on the one hand when it was cooled by its own evaporation until the tension of its vapour was only equal to that of the atmosphere, that is, to a temperature of $-181°$ according to Olszewski, and also when the temperature of the liquid was allowed to rise under pressure up to nearly the critical temperature. There appeared to be no appreciable difference in the absorption under these different circumstances when the oxygen was completely liquid, when it was near its critical temperature, and when it was completely gaseous; so far at least as concerns the three principal bands, which were all that could

* A Paper read before the Royal Society, June 20, 1889.

be seen in the light transmitted by the liquid in a thickness of 12 m.m.

It will be observed that taking the density of oxygen at $-181{\cdot}4°$ to be 1·124, as given by Olszewski, 12 m.m. of the liquid would be equivalent to 9·37 metres of the gas at atmospheric pressure — hardly more than half the thickness required to make A visible. The experiments, therefore, point to the conclusion that gaseous and liquid oxygen have the same absorption-spectrum. This is a very noteworthy conclusion. For, considering that no compound of oxygen, so far as is known, gives the absorptions of oxygen, the persistency of the absorptions of oxygen through the stages of condensation to the state of complete liquidity implies a persistency of molecular constitution which we should hardly have expected.

In order to compare the absorption of ozone with that of oxygen we employed a tube 12 feet long, made of tin-plate fitted with glass ends and coated with paraffin on the inside. We could not use the 18 m. steel tube on account of the action of the ozone on the metal, which rapidly reduced the proportion of ozone, and also because we could not conveniently cool it. Ozonised oxygen was passed into the tin tube for some time, while the ozoniser and the tube itself were cooled with ice and salt. The lime-light, viewed through the tube, looked very blue, and also the spot of light thrown from the tube on to a sheet of white paper was equally blue, indicating a considerable absorption of the less refrangible part of the spectrum. The absorption, so far as the visible rays are concerned, appeared to be of a general character, for the spectroscope revealed only four extremely faint absorption-bands. The centres of these bands were at about the wave-numbers 1662, 1752, 1880, and 1990, and their positions with reference to the bands of oxygen are indicated in the diagram. They were so faint as to be seen only with difficulty. When the hot carbon of an arc lamp was substituted for the lime-light they were rather more distinct, but the positions of the edges were undefinable. The light of a gas-lamp was insufficient to show them, and they were no better seen with a single-prism spectroscope of low dispersive power than with the spectroscope we employed for observing the oxygen. Only one of these bands, as shown by the diagram, is nearly coincident with an oxygen-band, namely, that near E, the faintest of the oxygen-bands. That at wave-number 1752 overlaps the strongest oxygen-band, but not at its strongest part, and has none of the peculiar character of its shading, abruptly increasing on the less refrangible side and slowly decreasing on the other side. Photographs of the spectrum (taken through a tube with quartz ends) showed that the ozone absorbed all the rays above the wave-number 3086—a point between Q and R—while partial absorption extended below Q. We may say, therefore, that we can trace no identity between the absorptions of ozone and those of ordinary oxygen. There is no mere displacement of the bands, such as we sometimes get when a coloured substance is dissolved in different menstrua, nor any such a resemblance as we have between the absorption-bands of the different cobaltous salts derived from different acids.

The four bands which we see to be produced by ozonised oxygen correspond fairly with the 2nd, 3rd, 5th, and 6th of the bands described by Chappuis as due to ozone (*Annales de l'Ecole Normale*, 2nd ser., vol. xi., May, 1882). These four bands, he says, are the first to be seen. We have failed to perceive any others with the 3·66 m. tube, though the oxygen was highly ozonised and maintained at at a low temperature. None of the bands were of sufficient intensity to make themselves visible on our photographic plates.

It will be noted that the absorption by ozone extends far below the limit of the solar spectrum. We found, however, that by diminishing the proportion of ozone to oxygen in the tube the limit of the transmitted light was continually advanced, as already described by Hartley. The limit of the solar spectrum may, therefore, very wel be determined by the average amount of ozone in the atmosphere, as Hartley supposes. The known variations in the limit of the solar spectrum may be taken as confirmatory of this hypothesis, although the comparatively small amount of these variations is certainly less than we should have expected if they measure the changes in the proportion of ozone in the atmosphere.

The absorptions of the class to which A and B belong must be those which are most easily assumed by the diatomic molecules (O_2) of ordinary oxygen. Whether oxygen in more complex molecules, as in ozone (O_3), may be capable of taking up the corresponding vibrations cannot easily be determined, because we cannot isolate ozone; but since none of the compounds of oxygen with nitrogen, hydrogen, or carbon, or, so far as known, with any other element, exhibit these absorptions, it is very probable that they are peculiar to the molecule O_2. From this point of view it will be interesting to determine—as we hope to do shortly—whether liquefied oxygen, which we suppose to have more complex molecules, produces these absorptions. The corresponding spectrum of emission has not as yet been observed, probably because the agency employed to render the gas luminous breaks up the molecules into single atoms of oxygen.

As for the other class of absorption, the diffuse bands, since they appear to have intensities proportional to the square of the density of the gas, they must depend on a change produced by compression. This may either be the formation of more complex molecules, as for example O_4, corresponding to the deviation from Boyle's law exhibited by oxygen gas, or it may be the constraint to which the molecules are subject during their encounters with one another. Increase of temperature would affect the former, tending to diminish the number of complex molecules formed at a given pressure, but would have no effect on the latter, for though the number of encounters of the molecules in a given interval of time would be greater the higher the temperature, yet so long as the volume was unaltered the ratio of the duration of an encounter to that of free motion would be sensibly unaltered. So far as any change due to temperature has been observed, it is that a rise of temperature slightly weakens the diffuse absorptions.

Reverting to the compounds of oxygen, none of them show the absorptions of oxygen, not even the general absorption of the ultra-violet rays. Some of them, such as water and carbon dioxide, appear quite transparent to ultra-violet rays, while in others, such as nitrous oxide, which show a general absorption of the ultra-violet rays, the limit of transparency is different from that of oxygen. In other respects we may say that there is no resemblance between the absorptions of the compounds of oxygen and those due to oxygen itself. Some of the former have very definite and characteristic absorptions, such as the well-known spectra of the peroxides of nitrogen and chlorine, and we must regard these as indicating the rates of vibration, which the molecules NO_2 and ClO_2 respectively are capable of easily taking up. The absence of the absorptions due to oxygen from all compounds of oxygen seems to indicate either that chemical combination is not, as has been supposed by some chemists, a temporary relation in which the molecular groupings are continually breaking up, to be formed anew with ever-changing elementary atoms; or, that the periods of dissociation are very small compared with the periods of association. For otherwise we should expect that such compounds of oxygen as CO_2 and NO_2 must always have amongst their molecules some molecules identical with those of oxygen and capable of taking up vibrations of the same period. At least we must conclude that little, if any, of the oxygen of these and other compounds is ever out of the influence of the other components.

We have re-examined the absorption-spectrum of N_2O_4 at various temperatures, and agree to the conclusion of Bell (*Am. Chem. Journ.*, vol. vii., p. 32) that N_2O_4, whether liquid or gaseous, effects only a general absorp-

tion at either end of the spectrum, and that the selective absorptions observed with it are due to the presence of NO_2.

In order to obtain pure N_2O_4, the tube in which the liquid was sealed was placed in a freezing mixture and a large part of the liquid frozen; the remaining liquid was then drained as completely as possible into the other end of the tube, and sealed off.

It should be observed that the crystals of N_2O_4 appear colourless, and that when they are melted the liquid and superincumbent vapour are of a very pale yellow colour. As the temperature rises both liquid and vapour become, as is well known, of a deep orange, and finally of a dark reddish brown colour. We examined the spectra produced by two thicknesses of liquid and vapour—(1) by that contained in a narrow tube about 1 m.m. in diameter, and (2) by that in a tube about 1 c.m. in diameter. At 15° to 20° the vapour in the narrow as well as in the wider tube showed the well-known absorption-spectrum of fine dark lines; no absorption by the liquid in the narrow tube could be detected, and the liquid in the wide tube showed no fine lines, but several faint, very diffuse bands, unresolvable into lines with a spectroscope of three prisms. These bands had their maxima in places where the fine lines of the vapour were most intense and most closely set, so that it might be inferred that they were due to similar molecules in both cases; but that in the liquid the vibrations of these molecules were no longer sharply defined, but modified by the constraint arising from the liquid state. Some parts, however, of the spectrum of the vapour, where the lines were closely set, did not appear to be represented by any definite bands in the liquid. The liquid absorbed a good deal of blue light in a continuous manner, while the vapour only absorbed it selectively. At the red end the limit of the visible spectrum was lower for the liquid than for the gas, that is, there was more absorption of red light by the vapour than by the liquid, so much so that below a certain point the absorption by the vapour appeared continuous.

The narrow tube was next immersed in a wider tube full of glycerin, which was gradually heated. As the temperature rose, the colour of both liquid and vapour deepened, the absorptions of the vapour were stronger, and the liquid gave the same bands as had been before observed with the greater thickness. At still higher temperature the absorption of blue light, both by liquid and vapour, diminished sensibly, until at 85° the groups of lines in the blue had pretty well disappeared from the spectrum of the vapour. In fact, at 85° there was no sensible difference between the actions of liquid and vapour on blue light, it seemed only some continuous absorption. At the red end the difference between the liquid and vapour remained quite as strongly marked as at lower temperatures: if anything, more so; and the absorptions in the orange, yellow, and green were unaltered. At 90° the lines of the vapour in the green began to fade, and at 100° they were very faint; but those in the orange, as well as the corresponding diffuse bands in the liquid, were as strong as before. There was still considerably more absorption of red light by the vapour than by the liquid, as if there were a strong absorption-band in the red of the vapour which was absent in the liquid.

As the temperature rose to 110° all the lines in the vapour had become faint, and at 115° they were no longer discernible, and there was no difference between the spectra of liquid and vapour except in the red, and even here the difference was less marked than at lower temperatures. At 130° no distinction was observable between the spectra of liquid and vapour; there were no lines or bands in either, but a good deal of general absorption. Liquid and vapour were dark, and appeared much of a colour, but the meniscus at the junction was quite evident. The tube was further heated to 155°, but no further change was noticed in the spectrum. On gradually cooling the tube, at 112° the least refrangible band in the orange was seen coming in both in vapour and liquid, diffuse in both. At 100° the usual lines were well seen in the orange, yellow, and citron of the vapour, faint lines in the green, and none in the blue; and subsequently the appearances presented on heating followed in the reverse order.

A solution of N_2O_4 in carbon bisulphide gave in a thickness of 7 or 8 c.m. diffuse absorption-bands in the green and citron, ill-defined as in liquid N_2O_4 and in corresponding positions. In a thickness of 1 c.m. these bands were no longer visible.

These observations bear out the supposition that pure N_2O_4 is without selective absorption of the visible rays, and that the absorption observed is due to NO_2, both in the vapour and liquid, this absorption being modified in the liquid by the state of solution, in which the molecules have much less freedom. As the temperature rises the proportion of NO_2 increases, and at the same time the density of the vapour increases and the freedom of motion of the molecules is diminished; they are less able to assume the more rapid vibrations, and those which they do assume become less sharply defined, so that the lines fade into bands and ultimately into a general absorption.

Taking Willard Gibbs's expression ("Equilibrium of Heterogeneous Substances," *Connecticut Acad. Trans.*, vol. iii., p. 239) for the density D, in terms of the pressure in atmospheres p, at temperature $t°$—

$$D = 3{\cdot}178 + \theta - \sqrt{\{\theta(3{\cdot}178 + \theta)\}}$$

where—

$$\log_{\cdot 10}\theta = 9{\cdot}47056 - \frac{3118{\cdot}6}{t+273} - \log_{\cdot 10}p,$$

as deduced from Deville and Troost's experiments, we find the density of NO_2 at 140° and 50 atmospheres, equal to 2, *i.e.*, equal to the density of N_2O_4 vapour at 60° and 1 atmosphere.

Dewar and Ansdell found the critical temperature for N_2O_4 to be 156°.

NOTE ON THE

THERMO-ELECTRIC POSITION OF PLATINOID.*

By J. T. BOTTOMLEY, M.A, F.R.S.,
and A. TANAKADATE, Rigakushi.

In carrying out a series of experiments on radiation of heat by solid bodies, an investigation to which one of the present writers has for some time past devoted considerable attention, it became necessary, for a purpose which need not here be detailed, to select a thermo-electric pair of metals, of which one metal is essentially platinum, as it passes through glass. Various pairs were considered, and some trials were made; and it was finally determined to make use of platinum and platinoid. The latter metal is an alloy whose electrical and mechanical properties were investigated some years ago by one of the present writers;† and since that time it has assumed considerable importance in the construction of electrical instruments and resistance coils. Partly on this account, and partly from present requirements, it became both interesting and necessary to determine the thermo-electric constant for a specimen of this alloy.

Platinoid is in composition very similar to German silver. In the manufacture of the alloy, however, tungsten is employed; and although an exceedingly minute quantity of metallic tungsten remains in the alloy, yet the properties of the substance are in many respects remarkable. The metal is capable of being polished so as to be almost as beautiful as silver in appearance, having only a slightly darker and more steel-like colour, and when it has been polished it remains absolutely un-

* A Paper read before the Royal Society, June 20, 1889.
† J. T. Bottomley, *Roy. Soc. Proc.*, 1885.

tarnished, even in the atmosphere of a large town, for years at any rate. It has very remarkable properties as to electric resistance. It possesses a higher resistance than any other known metal or alloy, while at the same time it has a very much lower temperature variation of electric resistance than any other known metal or alloy except platinum-silver alloy. It has also, as Sir William Thomson has found, very excellent elastic qualities.

Although it is not proposed to use the platinoid with any metal other than platinum in the investigation on thermal radiation above referred to, it nevertheless seemed advisable, when these experiments were being undertaken, to determine its position with respect to some other metals. It was accordingly tried as a pair with platinum, iron, aluminium, and with two specimens of copper.

A low-resistance Thomson's reflecting galvanometer was specially prepared for the purpose of the experiments. The mirror is a plane parallel mirror of very excellent quality by Steinheil of Munich. Its deflections were observed by means of a telescope with cross-wires and scale, instead of with lamp and scale. To avoid any influence of the suspending fibre (which, even though of single cocoon silk fibre, does, with short fibres, give an appreciable torsional resistance) the mirror was suspended by spider line. The suspending of a mirror, weighing with its magnet 0·2 grm., by a single spider line is a matter of some nicety and difficulty; but when it has been accomplished the result is so thoroughly satisfactory that it is easily admitted to be well worth a morning's labour.

To make the suspension, two small pieces of very thin bristle or of hard-spun silk fibre or split horsehair are attached to the ends of a suitable length of spider line recently spun by a good large* spider. By means of these attachments, which are easily seem, the spider line can be handled. It is then brought over the galvanometer mirror; and great assistance is experienced in these operations, and in operations with single silk fibres, by performing them on the top of a piece of looking-glass laid on the table. The illumination from beneath of the fibres makes it easy to do with these fine filaments that which it is otherwise scarcely possible. The fibre is attached to the galvanometer mirror with the smallest possible speck of shellac varnish, the greatest care being taken not to varnish any part of the spider line. When the varnish has dried the mirror can be lifted up by the spider line, caution being used at the moment of raising the one mirror off the surface of the other on account of the vacuum which is liable to be formed at the moment of separation. The mirror should be allowed to hang on the fibre inside a glass beaker for twenty-four hours at least, as the spider line stretches considerable for a time after the weight comes on it. A spider line which will carry a galvanometer mirror and magnet weighing 0·2 grm. may have, according to an estimate made by one of the present writers, about 1·700th of that of a single cocoon silk fibre.

For equal length and equal diameters the material of silk fibre has something like six and a half times the torsional rigidity of the material of spider line.

For the heating of the junctions a number of glass vessels were blown, resembling the flasks, with neck and condensing tube, used for fractional distillation, but with the condensing tube projecting upwards into the air, so that the steam of a liquid boiling in the flask ran back into the flask on being condensed. Into the shorter neck of the flask was introduced a cork which carried the thermo-junction and a mercurial thermometer, the thermo-junction being loosely bound to the thermometer, or, at any rate, kept in close contact with the middle part of the thermometer-bulb. The cool junction was bound to the bulb of a second thermometer, which dipped into a vessel containing water at the temperature of the laboratory. The water was kept thoroughly stirred from top to bottom by a properly arranged stirrer.

In the heating flasks the vapours of the following liquids were used:—Alcohol, water, chlorobenzol, aniline, methyl salicylate, and bromo-benzol.* The liquids were boiled vigorously, and the temperatures of the vapours were determined by means of mercurial thermometers. The mercurial thermometers were compared directly with the air thermometer.† The obtaining of a set of points of temperature by this means was very satisfactory in every case except that of the liquid of highest boiling-point, bromobenzol. In this case a curious phenomenon was observed. In spite of the fact that the vapour of the substance was rushing strongly into the condensing-tube and, indeed, out into the open air, at an elevation of 2 feet above the surface of the liquid, it was found exceedingly difficult to keep the temperature of the various parts of the boiling flask anything like uniform. The vapour formed itself into layers of different temperatures, the parts of the flask nearest the surface of the liquid being the hottest. At a height of 2½ inches above the surface of the liquid the temperature was often found to be as much as 8° or 10° C. cooler than it was just above the surface. The difficulty could, to a certain extent, be overcome by putting a cloak of fine flexible wire gauze all round the upper part of the flask; but the greatest watchfulness was needed to avoid mistakes.

In order to reduce the results obtained from the readings of the galvanometer to absolute electro-magnetic measure, a carefully prepared standard Daniell's cell was kept with its current always flowing through a known high resistance; and from time to time the galvanometer which was being used was thrown into the circuit, and the value of the galvanometer deflection determined. The electromotive force of the Daniell's cell was valued at 1·072 volts.

The results obtained are shown in curves and tables which accompany the paper.

In the curves the electromotive forces are shown as ordinates, the differences of temperature between the hot and cold junctions being indicated on the axis of abscissæ. The electromotive forces are given in C.G.S. units, and must be divided by 108 if it be desired to reduce them to volts. The differences of temperatures are given in centigrade degrees, and 0° C. is the lower limit as to temperature. The direction of the current in each of the cases represented is from platinoid to the second metal of the pair through the hot junction.

Table I. shows, in the way now well known,‡ the multiplier at any temperature centigrade which must be used as factor, with the difference of temperatures between the hot and cold junctions, in order to calculate the electromotive force in C.G.S. units. The algebraic sign corresponds with that used by Tait, and now adopted by Everett ("Units and Constants," 2nd Edition).

Table I.

Platinoid-platinum	$-925-1{\cdot}16\times t.$
Platinoid-aluminium	$-985-4{\cdot}31\times t.$
Platinoid-iron	$-2916+0{\cdot}86\times t.$
Platinoid-copper (A)	$-1246-5{\cdot}44\times t.$
Platinoid-copper (B)	$-1294-4{\cdot}88\times t.$

Combining the results of Table I. with those of Tait reduced by Everett, we obtain the thermo-electric distance of platinoid from lead, taken as zero, at various temperatures centigrade. If any one of the wires platinum, aluminium, iron, or copper used by us were identical with the wire of the same name used by Professor Tait, we should be able to deduce with exactness the distance of our platinoid wire from his lead wire. That, however, was not the case; and each of the secondary wires used

* The body about as large as a pea.

* Ramsay and Young, *Chem. Soc. Journ.* (*Trans.*), 1885.
† J. T. Bottomley, *Phil. Mag.*, August, 1885.
‡ Tait, *Edinburgh Roy. Soc. Trans.*, vol. xxvii., 1873, and Everett's "Units and Constants"—"Thermo-electricity."

by us gives us, as it were, a different result. Thus we have :—

Table II.

	Platinoid to lead.
From experiment with platinum	$-986-3\cdot26\times t$
,, ,, aluminium ..	$-1062-3\cdot92\times t$
,, ,, iron	$-1182-4\cdot01\times t$
,, ,, copper (A) ..	$-1110-4\cdot49\times t$
,, ,, copper (B) ..	$-1158-3\cdot93\times t$

Taking the mean of all of these, with the exception of the result for platinum, which we omit because different specimens of platinum are well known to differ thermo-electrically enormously among themselves, we obtain for the thermo-electric distance of platinoid from Professor Tait's lead wire $-1128-4\cdot1\times t$.

This result enables us to place platinoid in Tait's thermo-electric diagram. Its line is nearly parallel to those of palladium and German silver, and slightly above the latter. It is, however, to be remembered that, in all probability, different specimens of platinoid alloy would give results differing considerably from that quoted above.

Appendix. By A. Tanakadate.

The following experiment on the torsional rigidity of spider line was carried out in the Physical Laboratory of the Imperial University of Japan, 1884, and a notice of it was published in vol. ii. of *Rigaukkyokwai Tassi* ("Proceedings of the Science Society") of that year in Japanese. It has not hitherto been described in English, and the absolute determination as referred to below by Mr. T. Gray of the rigidity of silk fibre makes an estimate of the rigidity of spider line possible.

The determination of the torsional rigidity was a relative one, and the experiment essentially consisted in finding the deflection of a small magnet due to a given twist of the suspending fibre : the magnet being placed in the earth's magnetic field (0·3 C.G.S.). The deflection was observed by the usual method of the reflected image of a fine wire stretched before a lamp.

The mirror magnet was first hung by a silk fibre of 31 c.m. length, and placed in the usual way. The distance of scale from the mirror was 95 c.m. When the torsion head of the magnetometer was turned through one complete revolution (2π) in either direction from zero, the image of the reflected wire was displaced through 8 m.m. either way, or $8/2\times95=0\cdot0042$ radians, or 864″.

The silk fibre was now detached from the magnet, and a spider's line (newly spun) was attached in its stead. The length was 28 c.m., the magnetometer was put into its place, and the torsion head was turned as before, but no appreciable deflection could be observed, even when the torsion head was turned through ten complete turns (20π). It was suspected then that the mirror might have been caught against sides of its case ; a close inspection, however, showed that it was quite free. The fibre was then shortened to 2·3 c.m. (about one-twelfth its previous length), and the experiment was repeated. Ten complete turns of the torsion head gave a deflection of 1·5 m.m. or $15/2\times95=0\cdot00079$ radians, 16·5″.

In order to compare these deflections with each other, each deflection was reduced to that which would be given by a fibre of one c.m. in length by multiplying the deflections by the length of the fibre used. Thus, corresponding to the twist of one turn of the torsion head in a fibre of one c.m. long, we have :—

For silk fibre .. .. $864\cdot0''\times31=26800''$

For spider line .. .. $\frac{16\cdot5}{10}2\cdot3 = 38''$

From this we get the ratio of the torsional rigidity of spider line to that of silk fibre to be 1 : 710.

The diameters of the fibres were microscopically measured, and gave the following values :—

Silk fibre .. .. 0·00091 c.m.
Spider line .. .. 0·00028

If the elastic qualities of these fibres were the same, the ratio of the torsional rigidity would have come out $(28)^4:(91)^4$, 1 : 112 ; and hence the torsional rigidity of spider line is less than one-sixth of that of silk fibre of the same thickness.

The above result gives us only a relative value of the rigidities between the two fibres. If we take the mean value of the torsional rigidity of silk fibre to be 0·0012 C.G.S., as found by Mr. T. Gray,* the torsional rigidity of the spider fibre of the above experiment will be 0·0002 C.G.S.

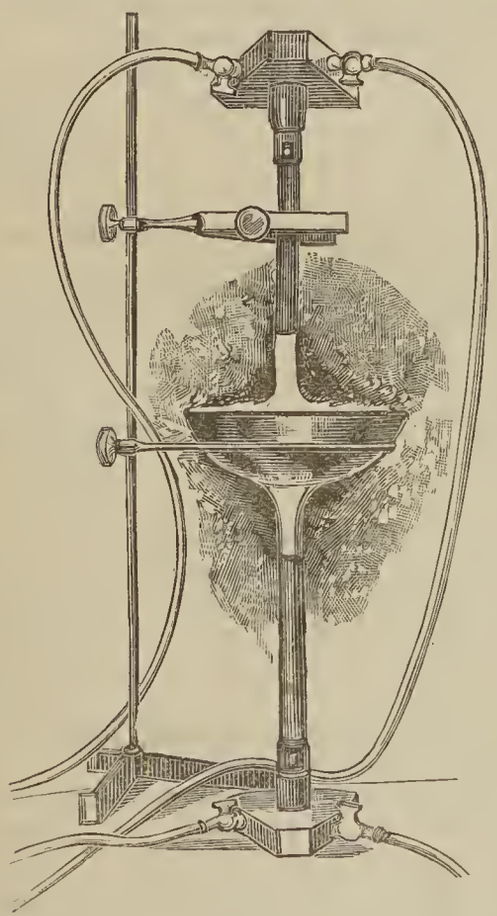
Mr. Gray's silk fibre may have had a slightly higher rigidity, as he states that it was boiled in water, while the fibre of the experiment just described was taken from those boiled in dilute potash water, as is the usual practice of preparing "mawata," which is very soft kind of silk.

SILICON IN PIG IRON.
DETERMINATION BY A METHOD OF RAPID EVAPORATION.

By Clemens Jones.

In the "direct process" of making steel, and very frequently when making foundry iron, it is necessary to determine silicon in the iron in a few minutes. To do this within the time-limit with reasonable accuracy has been found a task by no means simple.

By Ford's method, silicon can be determined in twelve minutes after taking the sample. There are several



modifications of this method, but each has the objection that during evaporation a loss is caused by spattering.

The endeavour to overcome this defect led to experiments on shortening the time by merely hastening the *modus operandi* of a standard method. Dr. Drown's admirable method was selected, and by the use of the device figured in the cut it was found that evaporation

* *Phil. Mag.*, 1887.

of 50 c.c. of nitro-sulphuric acid could be done in three minutes with complete dehydration of the silica, and very little loss, as evaporation is not carried to dryness. Moreover, the disappearance of nitric acid is marked by a strongly tinged flame reaction.

A platinum dish of 150 c.c. capacity is used. 1 grm. of borings is transferred to this, 50 c.c. nitro-sulphuric acid added, and the dish is then placed between the flames from two blast-lamps. The arrangement of the lamps calls for no description; a slight adjustment of the flames, in both distance apart and intensity, is all that is required before the right effects are secured. This being done, however, the arrangement becomes a fixture. The downward flame should be a trifle stronger than the upward one. In fact, wire gauze beneath the dish gives better results by distributing the heat evenly. A Bunsen burner may be substituted for the lower lamp. Violent ebullition is prevented by the current of heat and air upon the surface of the boiling liquid, so that by giving the dish a circular motion with a pair of tongs when nearing final expulsion of nitric acid the fumes of sulphuric acid are quickly obtained, accompanied by a sharp play of reddish yellow colour of the impinging flame. When finished, the sulphate of iron is in a thick semi-pasty state, into which hot water can be poured at once. Again placed between the flames, this is speedily dissolved and is ready for subsequent treatment.

I may add that gasolene gas was employed in the experiments.

A few comparative results are given below. The irons chosen were 1 low, 2 medium, and 1 high silicon iron. The slightly higher results by rapid evaporation are due to undissolved ferric oxide formed by the intense heat.

No. 2602. Regular method (Dr. Drown's). Silicon = 0·445 per cent. Rapid evaporation.

	C.c. acid.	Time for evaporation.	Per cent silicon.
1.	50	5 minutes	0·657
2.	50	4 ,,	0·639
3.	50	4 ,,	0·629
4.	25	2½ ,,	0·639

No. 3252. Regular method. Silicon, 3·858 per cent. Rapid evaporation.

	C.c. acid.	Time for evaporation.	Per cent silicon.
1.	50	5 minutes	3·863
2.	50	5 ,,	3·849
3.	50	3 ,,	3·765

No. 2074.

	Regular method.	Per cent silicon.
1.	,,	2·374
2.	,,	2·384

Rapid evaporation.

	C.c. acid.	Time for evaporation.	Per cent silicon.
1.	50	5 minutes	2·374
2.	50	5 ,,	2·328
3.	50	5 ,,	2·276
4.	50	4 ,,	2·320

No. 1967. Regular method. Silicon, 1·829 per cent. Rapid evaporation.

	C.c. acid.	Time for evaporation.	Per cent silicon.
1.	50	5 minutes	1·955
2.	50	4 ,,	2·058
3.	50	4 ,,	2·010
4.	50	5 ,,	1·810
5.	25	3 ,,	1·904
6.	50	3 ,,	1·913
7.	50	3 ,,	1·815

No. 4 of this series lost silica in igniting. No. 7 was completed in twenty minutes from the time of opening the balance case. Ten minutes was consumed in filtering, and the carbon burned off in the old way. By igniting with oxygen, and filtering more rapidly, the time for a complete determination can be undoubtedly reduced to fifteen minutes.—*Journal of Analytical Chemistry*, Vol. iii., Part 2, April, 1889.

DEPOSITS OF BARIUM SULPHATE FROM MINE-WATER.*

By FRANK CLOWES, D.Sc.,
Principal and Professor of Chemistry and Metallurgy in University College, Nottingham.

Specimens of remarkable deposits which have formed in the water-boxes of coal-mines in the neighbourhood of Newcastle-upon-Tyne have been for many years in the possession of the Museum of the Durham College of Science.

A rough analysis has been published by J. T. Dunn (*Transactions of the Newcastle Chemical Society*, vol. iii., p. 261) of an apparently similar deposit, which was formed during the autumn of 1876 in the Jane Pit at Walker. During this short period the sectional area of the box had been reduced by the deposit from seven and a half square inches to less than half a square inch, and had been in places almost completely closed. The deposit consisted of layers which were alternately white and brown, and was moderately soft. Analysis showed the percentage composition to be 90 of $BaSO_4$, 8 of $SrSO_4$, 1 of $CaSO_4$, the remainder consisting mainly of SiO_2, Al_2O_3, and Fe_2O_3. The water passing through the box at the time of the examination contained no trace of barium or of strontium.

Another similar deposit was found by Dr. Richardson (*Brit. Assoc. Report*, 1863) to contain about 90 per cent of barium sulphate and 3 of calcium sulphate, the remainder consisting of silica, alumina, ferric oxide, and moisture.

Professor Lebour states the pipes which convey water from the colliery workings of the Newcastle district are frequently entirely blocked in a short space of time with deposits, amongst which barium sulphate is seldom absent, and is often the chief constituent; and he draws attention to the fact that veins of barium sulphate are by no means uncommon in the coal measures of that district.

This deposition of barium sulphate is of interest in connection with the discovery of the sulphate as a cementing material in sandstone near Nottingham, and as no complete analysis existed of the water-box deposits in the Durham College Museum, Professors Bedson and Lebour have kindly furnished me with sections for chemical examination. The following results were yielded by the analyses:—

	Harton, box-deposit.	Jane Pit, Walker-deposit.	Newsham, box-deposit.
Loss at 100°	0·83	0·26	0·39
Loss by ignition . ..	2·15	1·51	1·95
$Fe_2O_3 + Al_2O_3$	5·44	0·12	0·37
BaO	56·72	61·30	61·09
SrO	trace	0·35	0·09
CaO	1·09	0·70	0·82
MgO	0·12	0·14	trace
SO_3	31·10	33·80	32·82
SiO_2	1·19	0·53	0·22
Alkalies, &c. (by difference)	1·36	1·29	2·25
$BaSO_4$..	86·37	93·35	93·03

The above deposits were mainly buff-coloured with thin layers of brown interposed; they were soft and loose, powder being easily detached by rubbing the surface with the finger. There was no appearance of crystallisation,

* A Paper read before the Royal Society, June 20, 1889.

but every indication of the deposit having been formed by rapid precipitation.

Professor Bedson (*Journ. Soc. Chem. Industry*, vol. vi., p. 712) and others have found barium chloride to be a common constituent of colliery waters of the district in which the above deposits have been formed. Relatively large quantities of the chloride have been found in some of these samples. The deposition may possibly arise from the admixture with such water of water containing sulphuric acid or ferrous sulphate, or both, since these substances are constantly formed by the oxidation of pyrites in the coal or in the associated shale beds. Or the barium sulphate occurring in veins in the coal measures may pass into solution under conditions yet unknown, and be deposited again as such.

Bischof mentions that hot springs may contain $BaCO_3$ and Na_2SO_4 together in solution; since at high temperatures these substances do not undergo double decomposition. Such a spring water will, however, deposit $BaSO_4$ as it cools, since at ordinary atmospheric temperatures $BaSO_4$ and Na_2CO_3 are produced by the interchange of constituents. Possibly alteration of temperature may in a similar manner give rise to the above remarkable water-box and pipe deposits.

Possibly the deposition of barium sulphate in the form of stalactite, which has occurred in some parts of Derbyshire, may be due to the same causes as these mine-water incrustations.

DETECTION AND DETERMINATION OF SODIUM HYDROCARBONATE IN MILK.

By L. PADÉ.

Sodium hydrocarbonate is the salt most commonly added to milk to prevent coagulation. In more than a hundred experiments with pure milks the author has found that a drop of decinormal sulphuric acid was always sufficient to render the ash of 10 c.c. of milk acid. It might seem, therefore, that by determining the alkalinity of the soluble ash of a milk we might determine the hydrocarbonate added. The author has, however, never reached this result, and according to his experiments in pure milk, mixed with 1 grm. per litre of sodium hydrocarbonate, we never find more than 0·34 to 0·40 grm. of alkalinity calculated as sodium hydrocarbonate. This process, therefore, though sufficient for detecting the presence of the salt, has no value for its determination. When seeking the causes of the disappearance of the greater portion of the alkalinity of the soluble ash of a milk containing sodium hydrocarbonate, the author has found an exact process for the determination of the salt. During the ignition about two-thirds of the sodium carbonate are transformed into sodium phosphate and calcium carbonate by reacting upon the calcium phosphate of the milk. Hence the ash of a milk to which sodium hydrocarbonate has been added contains sodium phosphate. But as the soluble ash of a pure milk is very slightly alkaline, and contains only traces of phosphoric acid, it is sufficient, in order to find exactly the quantity of sodium hydrocarbonate which has been added, to take the alkalinity of the ash and determine the phosphoric acid which they contain.

To effect these two determinations the author has arrived at the following method:—

He incinerates 25 c.c. of the milk and determines the alkalinity with decinormal sulphuric acid; the volume obtained in c.c., multiplied by 0·0084 grm., gives the quantity of hydrocarbonate not transformed into sodium phosphate contained in 25 c.c. of milk, and on afterwards multiplying by 0·0336 we obtain the percentage. In this neutral solution, mixed with 2 c.c. of a slightly acetic solution of sodium acetate at 10 per cent, the phosphoric acid is determined by means of standard uranium acetate.

The uranium solution is standardised so that 1 c.c. corresponds to 0·01 grm. of sodium hydrocarbonate in 100 c.c. of milk when the determination is effected in 25 c.c.

The standard of the liquid is derived from the transformation of sodium hydrocarbonate into phosphate according to the following formula—

$$4(CO_3NaH)+(PO_4)_2Ca_3= \\ =2PO_4Na_2H+3CO_3Ca+CO_2+H_2O,$$

according to which 336 grms. sodium hydrocarbonate yield 284 grms. sodium phosphate, or for 1 grm. of hydrocarbonate, 0·84523 sodium phosphate containing 0·4226 grm. phosphoric acid (P_2O_5).

The uranium liquid is standardised, volume for volume, with a solution containing, per litre, 3·11 grms. sodium-ammonium phosphate. This weight of sodium phosphate is equivalent to 2·5 grms. sodium hydrocarbonate. Then, if we make the determination upon 25 c.c. of milk, 1 c.c. of the standard solution of uranium or of sodium phosphate answers to 0·01 grm. hydrocarbonate in 100 c.c. of milk.

The determination is made in the ordinary manner, either by spotting with ferrocyanide or by means of tincture of cochineal. The latter process is the more sensitive, on account of the dilution of the uranium liquid.

On adding to the weight per cent of alkalinity as found that given directly by the determination of the phosphoric acid, we obtain the total percentage weight of the sodium hydrocarbonate added to the milk. The greatest irregularity the author has ever observed in using this process has been an excess of 0·008 grm. of hydrocarbonate per cent.—*Comptes Rendus*, cix., p. 154.

ON THE AMMONIO-COBALTIC TUNGSTATES AND VANADATES.

By ADOLPHE CARNOT.

A solution of ammonium tungstate, poured into a dilute solution of a purpureo-cobaltic salt acidified with acetic acid, produces at once an abundant rose-coloured precipitate analogous to that produced by the molybdate. When the reagent has been employed in sufficient quantity the liquid gradually becomes clear and colourless; it no longer contains nickel and gives no black deposit with ammonium hydrosulphate. The rose-coloured precipitate, if dried at 100°, turns lilac; if heated progressively to redness it loses water, ammonia, and oxygen, and passing through dark blue and blackish green tints, it finally becomes light greenish yellow. It remains infusible and undecomposable at a bright red heat. When cold, the ignited matter is of a greyish blue. It answers to the formula $CoO,5WO_3$. The analysis of the precipitate when merely dried gave $Co_2O_3,5NH_3,10WO_3+9HO$.

The salts of cobaltous and nickelous oxides are not precipitated under the same circumstances by the tungstate. This reaction might therefore serve for the separation of the purpureo-cobaltic compound, as it has been already indicated for the molybdate. But it is more difficult to obtain a product of unvarying composition. On the one hand, ammonium tungstate being sparingly soluble in water at the common temperature (1 part in 32), and much more soluble at 100°, we are in danger of producing a deposit of this tungstate, and consequently an excess of the ignited product if we employ a solution recently prepared. If, on the other hand, the solution is not sufficiently acid, there may be produced a crystalline deposit of cobaltous or nickelous tungstate, both causes of error, of which there is less risk in using the molybdate.

In ammoniacal liquors the reactions of the cobalt and

nickel salts are quite different with the tungstate than with the molybdate. A purpureo-cobaltic salt gives an insoluble rose precipitate in presence of a slight excess of ammonia as well as in an acetic liquid. A cobaltous salt gives a crystalline precipitate of a yellowish grey, which alters on exposure to the air and becomes rose on drying. This is a double ammonium-cobalt tungstate—

$$15WO_3.2CoO.8NH_4O+3HO.$$

A nickel salt gives a crystalline precipitate of a slightly bluish tint, which is formed slowly. Along with it ammonium tungstate is often deposited in white needles.

Vanadates.

Ammonium vanadate produces with ammonio-cobaltic salts in a slightly acetic solution an orange-yellow precipitate which answers to the formula—

$$Co_2O_3.5NH_3.5VaO_5+9HO.$$

This compound, if carefully heated to dull redness, becomes agglomerated and swells up much. It takes at the same time a blackish grey tint, which in a short time passes to a rose-brown. If heated above dull redness the product melts completely and becomes blackish. After and before fusion its composition is $2CoO.5VaO_5$.

The cobaltous and nickelous salts form slowly a crystalline deposit in an acetic liquid, but they are at once precipitated on saturating the liquid with ammonia.

Cobalt yields under the same conditions a green precipitate of cobaltous vanadate, which is readily peroxidised by the air and becomes yellow. If dried to 100° it takes a reddish brown tint, and yields, on fusion, a black compound, CoO_2VO_5.

Nickel gives an orange-yellow precipitate which turns brown when dried at 100° and black on fusion—$NiO,2VO_5$.

This nickel divanadate is very easily obtained on saturating with a slight excess of ammonia a solution which was originally acetic, and, in consequence, of a brown colour. A monovanadate, NiO,VO_5, may be obtained less easily on using a larger quantity of ammonia. No precipitate appears if we use a colourless vanadate, neutral or slightly ammoniacal, pouring it into a solution of nickel, likewise ammoniacal.

There appears to be formed by the action of free acetic acid a deeply coloured ammonium divanadate, which, in presence of a salt of nickel, yields, on saturation with ammonia, a precipitate of nickel divanadate.—*Comptes Rendus*, cix., p. 147.

ON PRECIOUS STONES.*

By GEORGE F. KUNZ

(Continued from p. 71).

Foreign Sources.

In this, the fifth of the annual reports on precious stones in the United States, which have done much toward awakening a wide-spread interest in American gems, it was thought well to give a brief sketch of some of the most important changes which are taking place in precious stones at the principal sources, which are usually foreign.

Diamonds.—The author of the "Arabian Nights" undoubtedly thought that he was imagining the wildest and most improbable things when he described the collection of such treasures in the Valley of Diamonds by "Sinbad the Sailor." Yet when compared with the African mines this profusion of wealth has paled into utter insignificance. A glimpse at these new valleys of diamonds will be interesting. The primitive method of washing was carried on for centuries by thousands of slaves, who, like those who built the pyramids, were driven by a master mercilessly goading them on, whip in hand. To-day we have the most ingenious and powerful machinery, which allows fewer diamonds to escape than would the keenest and most disciplined army of washers.

At the Kimberley diamond mines in South Africa wonderful progress has been made in the last decade. About 1877 the work of consolidating the different companies began. Originally the mines were worked as 3238 separate claims, each 31 feet square, with a 7½ foot roadway between every two claims; now these are all united in about forty companies. A mine in the early days was a bewildering sight. Miles of wire cables running from individual claims were stretched across it in all directions; to these were attached the buckets for carrying the earth, reef, or wall rock of the mines, and at times water. Some of the claims were almost level with the surface, while others next to them might be cut down 200 feet, and others only 100 feet, yet all being worked independently. At the sides were endless belts with pockets for carrying the earth. One of the results of this independent system of working was that rock was dropped so recklessly that it is said to have been as dangerous as the battlefield to stand around the edges of the claims. Not only was the loss of life great from this source, but also from the falling of immense masses of reef, loosened by the blasting, which sometimes buried a score of men at once. But improved methods were gradually introduced. Steam railroads were run into the mine, and parts of it were levelled down. Millions of tons of reef required removing, and the only way to accomplish this was to assess every company in the mine proportionately. At first many mistakes were made, if mistakes they can be called when the problems offered for solution were entirely new and untried. The yellow or surface soil which overlaid the blue stuff pulverised so readily that it could be taken to the washing machine direct; but as the claims were extended down into the blue rock this proved harder, and dynamite became necessary. Immense quantities of it are now used for blasting. Through careless storing, 30 tons of dynamite, 10 tons of blasting-powder, and gelatin, in all worth 80,000 dollars, exploded on January 10, 1884, with terrific effect; the smoke column, 1000 feet high, was visible at the River diggings, 35 miles distant.

After the earth is raised it is put on the sorting ground, where it is partially disintegrated by water and the action of the atmosphere. It is then further broken up by hand and taken to the "compound" or diamond-sorting machine. After being more finely broken up it is passed down into large vats containing immense centrifugal wheels, by which, as they rapidly revolve, the rock is finely divided. The lighter minerals, such as quartz, mud, and mica, are then floated out, while the diamonds, garnets (some of which are exceedingly rich in colour, and of large size, and are sold under the name of cape rubies), and other heavy minerals, are concentrated in the lower part of the "compound." So thoroughly does this pulverise the rock and earth that all the diamonds, even those of the size of a pinhead, are saved.

A prize of £5000 was offered for the best tunnel or shaft system for use at the Kinberley mines, and the prize was awarded to the Jones system, which is sunk on the coffer-dam principle. At present there are seven shafts and inclined planes in the Kimberley mine alone, all sunk at some point in the reef outside of the mine. From 11,000,000 to 13,000,000 gallons of water are annually hoisted from the Kimberley mine at a cost of sixpence per load of 100 gallons.

In addition to many miles of aërial tramways, there are over 170 miles of tramway around the four Kimberley mines, 2500 horses, mules, and oxen, and 350 steam-engines, representing 4000 horse-power, are employed in the works. For labour, £1,000,000 are annually expended, and over £1,000,000 for fuel and other supplies. The gross capital of the companies is nearly £10,000,000. Over 10,000 natives, each receiving £1 per week, and

* Abstract from "Mineral Resources of the United States."

1200 European overseers at an average wage of £5, are employed. It is now proposed to consolidate all the companies into an enormous diamond trust, with a capital of £10,000,000, but at the present quotations of the shares of the company they are valued at over £14,000,000. The supposition long held that this unification would ultimately be accomplished is partly confirmed by the report, this spring, that the house of the Rothschilds, of London, is about to put in operation a project for the consolidation of the diamond mines into one gigantic trust for the regulation of prices and production.

The South African mines yielded during the last ten years 27,878,587 carats, valued at £31,717,341. The yield for 1887 was 3,646,899 carats, worth £4,033,582 at a valuation of £1 2s. 1½d. a carat. In December, 1887, a single sale of rough diamonds was recorded of £150,000, and in February, 1888, of £250,000, or 750,000 dollars and 1,250,000 dollars, respectively. The average value of a carat of diamonds for some years from the respective mines has been as follows:—

Average Value of a Carat of South African Diamonds.

	s.	d.
Kimberley mine	17	6¼
De Beers mine	17	8
Bultfontein..	18	2½
Dutoits Pan	24	7¼
River digging	47	6

The product of the latter mine, while only $\frac{1}{125}$ of the weight in carats, was worth $\frac{1}{62}$ of the entire product, the stones averaging much finer quality.

The approximate annual yields for the last ten years have been as follows:—

Years.	Carats.	Value.
1878	2,540,000	£2,672,734
1879	2,610,000	2,864,631
1880	3,030,000	3,168,000
1881	3,315,000	4,200,000
1882	2,385,000	3,500,000
1883	2,312,000	2,359,466
1884	2,204,786	2,228,678
1885	2,287,263	2,228,680
1886	3,047,639	3,261,570
1887	3,646,899	4,033,582
River digging	500,000	1,200,000
Total	27,878,587	31,717,341

Not only has the yield of the African mines been great, but the diamonds have been of much larger average size than those from any of the old mines. The finding of a 17-carat stone in the Brazilian diggings was sufficient to secure the freedom of the fortunate slave who found it; but stones of this size are found by the hundred here. A 100-carat stone scarcely creates as much excitement as a stone of one-fifth the size did in Brazil.

It is estimated that from one-fifth to one-quarter of all the yield never reached the proper owners, as the native diggers swallow and conceal the diamonds in every possible manner. Hence it became necessary for the companies, in self-defence, to take extraordinary precautions against this great loss, and overseers or special searchers were appointed, who made the most thorough examination of all who left the mines. The natives use most ingenious methods for the concealment of the gems. On one occasion some officers, suspecting that a Kaffir had stolen diamonds, gave chase and caught up with him just after he had shot one of his oxen. No diamonds were found upon the Kaffir, it is needless to say, for he had charged his gun with them, and after the disappearance of the officers he dug them out of his dead ox. Diamonds have been fed to chickens, and a post-mortem recently held over the body of a Kaffir revealed the fact that death had been caused by a 60-carat diamond which he had swallowed. Early in the history of the mines a detective force, consisting of men, women, and children, was formed, and the severest punishment is still inflicted on transgressors of the Diamond Act. None but those authorised by law, termed patented agents, less than fifty in number, are allowed to purchase, or even to possess, rough diamonds at Kimberley.

The actual loss of diamonds would not have been so great but for the irregular diamond buyers, or "I.D.B's.," as the "fences" are called, who sent the stones to England and undersold the company in the London market. It was a question at one time whether the mines could be profitably worked under such disadvantages. Within the last two years, however, this pilfering has been in great measure checked by the adoption of what is known as the compound system, by which the "boys" are housed and fed under contract for a certain term, provided with amusements and liquor, and thus kept apart from the influences of the vicious whites. Now the visitors who buy from natives diggers what they suppose to be valuable diamonds and secrete them until they have passed beyond the reach of the officials, find to their disgust that they have purchased fac-similes in glass, perfect even to the characteristic yellow tint peculiar to many diamonds from this locality.

Diamonds weighing 38,000,000 carats, or over 7½ tons, have been found here. In the rough their aggregate value is £50,000,000, and after cutting £100,000,000, or nearly 500,000,000 dollars more than the world's yield during the two preceding centuries. Of the whole yield not more than 8 per cent can be said to be of the first water, 12 per cent of the second water, 25 per cent of the third, while the remaining 65 per cent is called bort, a substance which, when crushed to powder, is of use in the arts for cutting hard substances and engraving. This must not be confounded with the carbon (carbonado) found in Brazil, an uncrystallised form of the diamond, which, from its structure, is adapted for use in drills for boring and tunnelling rocks, &c., and has never yet been found in South Africa. It is worth from six to ten times as much as bort.

More diamonds weighing over 75 carats after cutting have been found since the African mines were opened than were known before. The Victoria, the Great White, or the Imperial Diamond, is supposed to be from South Africa. Concerning its early history very little is known; in fact, where the stone was found is only a matter of conjecture—a remarkable circumstance when we consider that it is the largest brilliant in the world. The original weight of the stone was 457½ carats, or $3\frac{1}{10}$ troy ounces; after cutting, 180 carats, valued at £100,000.

On March 28, 1888, there was found in the De Beers mine an octahedral crystal of diamond weighing 428½ carats; it is not entirely white, having a slight yellow tinge. It was valued at £3000. From its form it is believed that it will cut into a brilliant of 200 carats, hence it will be the largest known.

Production of Diamonds at the Griqualand West Mines, Kimberley, De Beer's, Dutoits Pan, Bultfontein, and St. Augustine, from September 1, 1882, to December 31, 1887.

Years.	Carats.	Value.	Average per carat.	
		£	s.	d.
1882, four months..	856,353⅜	1,119,210	26	1½
1883	2,312,234⅛	2,359,466	20	4¾
1884	2,204,786½	2,562,623	23	2¾
1885	2,287,261	2,228,678	19	5¾
1886	3,047,639¾	3,261,574	21	5
1887	3,646,899¾	4,033,582	22	1½
Total	14,355,174½	15,565,133	21	8¼

Comparative Yearly Exports of Diamonds from January 1, 1883, to December 31, 1887.

Years.	Carats,	Declared value. £	s.	d.	Average per carat. s.	d.
1883	2,413,953⅜	2,742,521	1	0	22	8⅝
1884	2,263,686⅝	2,807,288	3	4	24	9½
1885	2,440,788⅛	2,492,755	13	2	20	5
1886	3,135,432¾	3,507,210	14	0	22	4
1887	3,599,036¼	4,251,837	14	6	23	7½
Total ..	13,852,897⅛	15,801,613	6	0	22	9¾

Imports of Diamonds into Kimberley from the River Diggings, from September 1, 1882, to December 31, 1887.

Years.	Carats.	Value. £	Average per carat. s.	d.
1882, four months ..	5,742⅜	6,010	20	11⅛
1883	14,800⅜	37,112	50	1¾
1884	19,710⅜	57,639	58	5⅔
1885	27,992	56,123	40	1⅛
1886	38,673⅞	84,829	43	10¼
1887	46,171½	95,433	41	4⅛
Total	153,090½	337,146	44	0½

Summary of Imports of Diamonds into Kimberley from September 1, 1882, to December 31, 1887.

Whence imported.	Carats.	Value. £	Average per carat. s.	d.
Colony, England, &c. ..	130,133½	127,831	19	7¾
Orange Free State ..	306,660⅝	505,428	32	11½
River diggings (Barkly West)..	153,090½	337,146	44	0½
Total	589,884⅝	970,405	32	10¾

Summary of Production of Diamonds at the Griqualand West Mines for the Year 1887.

Mines.	Carats.	Value. £	s.	d.	Averege per carat. s.	d.
Kimberley ..	1,333,832½	1,410,207	12	1	21	1¾
De Beer's ..	1,014,048	1,022,878	6	5	20	2
Dutoits Pan ..	696,576¼	987,283	17	8	28	4⅛
Bultfontein ..	602,246	612,962	18	6	20	4¼
St. Augustine.	197	250	0	0	25	4½
Total ..	3,646,899¾	4,033,582	14	8	22	1½

Produetion of Diamonds, Kimberley Mine, from September 1, 1882, to December 31, 1887.

Years.	Carats.	Value. £	Average per carat. s.	d.
1882, four months..	380,955¼	456,420	23	11½
1883	947,817⅜	846,705	17	10¼
1884	642,438	634,332	19	9
1885	523,774½	458,858	17	6½
1886	889,864	883,503	19	10¼
1887	1,333,832½	1,410,207	21	1¾
Total	4,718,681⅝	4,690,025	19	10½

The diamond mines at Salabro, Brazil, known as the Canavieiras, were discovered in 1882 by a poor miner who had worked in the earlier mines, now nearly exhausted. They are situated at a distance of two days' journey from Canavieiras, near the river Pardo, and the gems are found at a depth of about 2 feet in a red gravel. They are very fine in quality, and are remarkable for their purity and whiteness, the crystals being of such a form that scarcely any cleaving is necessary.

History repeats itself, and as, when the Brazilian mines were first discovered, they sent the stones to India to enter the European markets in European wrappers, so Bultfontein diamonds were sent to Canavieiras to be shipped to Europe as the product of that mine.

So great was the rush for these mines at first that, notwithstanding the rumours of a malarial climate and epidemic diseases, by the end of the first year 3000 miners were at work where shortly before was a virgin forest. For a time even this number was exceeded. The other Brazilian mines have been only slightly worked of late years.

The recent concentration of some of the diamond mining companies in South Africa in their efforts to regulate the production and price has led to an increased interest in mines located in Brazil and India. During the past year the Madras Presidency Diamond Fields Company (Limited) has been organised with a capital stock of £190,000. To prove that the Indian mines are not yet exhausted, operations will be commenced at the Wadjra Karur field in the Madras presidency. On this field of 554 acres was found a very fine 67½ diamond crystal which furnished a 25-carat stone, called the Gow-do-Norr, valued by the company at £15,000. An English company has recently been formed, under the name of the "Hyderabad Deccan Mining Company," to work the mines in Krishna Valley, India, where it is thought the famous Koh-i-noor was found.

Diamonds have been found in the Tertiary gravels and recent drift near Bingera, in Inverell, Australia; also along the Cudgeon river, 160 miles north-west of Sydney, and in other districts. The colours are white, straw, yellow, light brown, pale green, and black. The largest stones yet found were cut into gems weighing 3½ and 3 carats, respectively. A trial made by the Australian Diamond Mining Company produced 190 diamonds, weighing 197¾ carats, from the washing of 279 loads of earth. These Australian fields can scarcely be called productive as yet, nor from present appearances do they seem likely to become formidable competitors of the South African fields.

India, Borneo, and Australia are now yielding very few diamonds, probably not more than 1 per cent of the entire product. These three countries, together with Brazil, yield probably less than 10 per cent of the total output.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 5, July 29, 1889.

A New Process for the Volumetric Determination of Silver, Mercury, and Thallium by Means of Potassium Iodide.—Adolphe Carnot.—This paper will be inserted in full.

Researches on the Sulphites.—P. J. Hartog.—The author has formed the potassium-, the sodium-, and the normal double potassium-sodium salts, and studied them chiefly from a thermo-chemical point of view.

Synthesis of Some Selenium Compounds of the Aromatic Series.—C. Chabrié.—The author has undertaken the synthesis of compounds in which the selenium is directly combined with the carbon of the cyclic nucleus. The chloride, $SeCl_4$, reacts upon benzene, yielding the subchloride and the mono-, bi-, and trichlorobenzenes, which are separated by water from the subchloride. The chloride, which chlorinises benzene and toluene, acts in a similar manner upon the fatty carbides. In presence of aluminium chloride $SeCl_4$ yields with benzene selenophenol, phenyl-selenide, and a red oil which distils at 245° to 250°, and has the composition $Se_2(C_6H_5)_3C_6H_4Cl$.

Selenium does not react upon benzene in presence of aluminium chloride, as do oxygen and sulphur.

The Oxidising Action of Nitrosocamphor under the Influence of Light.— P. Cazeneuve.— Nitrosocamphor is decomposed under the influence of light. If dry it yields nitrous gas. If mixed with water it gives off pure nitrogen, and oxidises, at the same time, bodies with which it comes in contact. The author has studied this phenomenon in the cases of alcohol, mannite, glycerin, and the oxalic and formic acids. The facts observed may be compared with certain chemical actions in plants. The formation of chlorophyll and of the colouring-matters of flowers which appears connected with the intervention of light, may be the result of oxidising actions effected by the intervention of oxygen compounds decomposable by light.

On the Isocamphols. Influence of Solvents upon their Rotatory Power.—A. Haller.—The modifying power of solvents, if null in case of any given body, may be exerted upon one or several of its isomers. In the case of certain racemic compounds it may throw a light upon the nature of the compounds which concur in the formation of these optically inactive bodies.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 3.

Contributions to Technical Gas-Analysis. — Clemens Winkler.—This memoir will be reproduced at length as early as possible.

The Density-numbers Discovered by J. A. Groshans.—Dr. G. Th. Gerlach.—Concerning this important paper we can at present merely say that the term density-number does not mean the same as density or specific gravity. The author has expressed the view that with the exception of H, C, and O probably every element consists of several micro-particles, and that of such chlorine has 4, bromine 9, and iodine 15.

Convenient Preparation of Chromium Chloride.— A. Vosmaer.—The author obtains Cr_2Cl_6 in any desired quantity by passing chlorine gas over heated chrome iron. In a combustion-tube the product can easily be obtained pure, as the ferric chloride is much more volatile and the manganous chloride much less volatile. The author uses a chrome iron containing about 21 per cent of chromium. Care must be taken that the tube does not become blocked up. The product obtained was quite insoluble in water, and consisted of long beautiful violet needles of a velvet-like lustre. The author attempted to obtain tungsten hexachloride in a similar manner from tungsten-iron. The result was a mixture of scarlet needles of $WOCl_4$ and of yellow WO_2Cl_2. The former compound passes quickly into the latter.

Determination of Silicon and Iron in Cryolite.—R. Fresenius and E. Hintz.— The authors attempted the solution of this question by decomposing the samples with sulphuric acid in a suitable apparatus and conducting the volatile products, hydrogen fluoride and silicon fluoride, into ammonia. The bulk of the silicon, however, remained in the residue in the form of fine sand, and only relatively small quantities were volatilised. The following method was used with success. The apparatus employed was a stout lead tube,, of 2·6 c.m. internal diameter, bent U-shape, and with its lower curved part completely bedded in a sand-bath. The two limbs of the tube were closed with perforated caoutchouc stoppers, in each of which a smaller lead tube was fixed air-tight. One limb was thus connected with a sulphuric acid washing-bottle, whilst to the other were joined two other lead tubes similar to the decomposition-tube, but having only an internal diameter of 2 c.m. The furthest of these tubes was again connected with a glass U-tube containing water and with an aspirator, so that a slow current of air can be drawn though the apparatus. Before using, the decomposition-tube may be charged with water and heated to 200° C., so that its inner surface may become covered with lead sulphate. After this it may be washed with water and is ready for use. The two narrower leaden tubes of the apparatus are then charged with ammonia; a weighed quantity of the cryolite—say 5 grms. —is introduced into the decomposition-tube, covered with 15 c.c. of undiluted sulphuric acid, and the apparatus is closed air-tight. The aspirator is set in action so that a slow current of air passes through the apparatus; the sand-bath is heated to 200°, the temperature being indicated by a thermometer plunged into the sand-bath. After heating for two hours and keeping up the current of air the apparatus is let cool, the contents of the decomposition-tube are rinsed out into a platinum vessel, and compounds of alumina, &c., are dissolved by the application of heat, and, if needful, by the addition of a few drops of hydrochloric acid. The residue, containing the bulk of the silica, is filtered off, washed, and melted with sodium carbonate. As the residue possibly may not be quite free from fluorides, the alkaline reaction of the watery solution of the melt is almost entirely but not quite neutralised at a boiling heat with hydrochloric acid, and the silica is chiefly separated out by evaporation. To the filtrate there is now added a solution of zinc carbonate in ammonia, and the liquid is concentrated until all ammonia is expelled. The separation of silica from the last precipitate is effected in the known manner by solution in nitric acid, evaporation, re-solution in nitric acid, and filtering off the residual silica. The part of the melt which is insoluble in water is dissolved in silica, and here also the silica is determined in the usual manner. The portions of silicon have still to be determined which were volatilised as silicon fluoride, and retained in the lead tubes charged with ammonia. On emptying the tubes the ammoniacal liquid was found turbid from the presence of lead sulphide and sulphate, both arising from the previous treatment of the tube with sulphuric acid. Lest small quantities of silica should escape determination this precipitate is filtered off, ignited along with the filter, the ash evaporated down with a few drops of nitric and sulphuric acids, and the lead sulphate thus formed is extracted with ammonium acetate. Any residue is added to the silica to be weighed. The ammoniacal solution is mixed with so much sodium carbonate that, after the expulsion of the ammonia, the reaction may still be distinctly alkaline, and here, as above, the silica is separated by means of an ammoniacal solution of zinc. The four or five portions of silica are weighed together and tested as to their purity by volatilisation with sulphuric and hydrofluoric acid. Iron in cryolite is determined by dissolving in sulphuric acid and filtering off the insoluble residue. This residue is fluxed with sodium carbonate, the melt is softened with water, the silica is separated with hydrochloric acid, the hydrochloric and sulphuric are mixed together, and the iron present in solution is per-oxidised, if needful, with chlorine-water. On pouring this liquid into strong hot potassa-lye there is obtained a small precipitate, which is washed and dissolved in hydrochloric acid. After the addition of tartaric acid pure iron sulphide may be precipitated by means of ammonia and ammonium sulphide, converted into ferric oxide in the ordinary manner, and weighed.

Examination of Vermicelli for Foreign Colours.— L. Cavedoni (*L'Orosi*).— 100 grms. of the sample are dried, powdered, treated with 200 grms. alcohol for twenty-four to thirty-six hours, and the filtrate is concentrated to 10 c.c. If saffron is present the extract is yellow and has an odour of saffron. The yellow colouring-matter of safflower does not dissolve in alcohol. The yeliow of turmeric is taken up by alcohol, and the extract smells of turmeric. Coal-tar colours dissolve in alcohol, and can be extracted from the concentrated aqueous residue by amylic alcohol. If Martius yellow is present the aqueous extract is decolourised by hydrochloric acid and the yellow colour is restered on neutralising with ammonia.

A Substitute for the Calcium Chloride Tube in Organic Analysis.—Jos. Preusser.—The apparatus cannot be intelligibly described without the accompanying figure.

The Determination of Thallium and Mercury.—Dr. W. Feit.—Thallium is generally determined by precipitation as thallous iodide, which is then dried at 110° to 120° on a weighed filter and weighed. The results agree well together, but they are rather too low, as the iodide is not absolutely insoluble, even in acetic or ammoniacal water. The author proposes a method founded on the reaction of the salts of thallium oxide with potassium iodide. If the solution of a thallic salt is mixed with potassium iodide there is a greenish black precipitate consisting of a mixture of thallous iodide and free iodine. The liberated iodine is converted into hydrogen iodide by an excess of arsenious acid and the excess is titrated back with iodine solution. For the execution of the analysis the author uses a solution of arsenious acid approximately decinormal and an approximately 1-50th normal solution of iodine accurately standardised with this solution. To prepare the arsenious solution 4·942 grms. of arsenious acid are dissolved in an excess of alkali in a litre flask, neutralised with hydrochloric acid, and filled up to the mark with sodium hydrocarbonate. The standardising is effected with absolutely pure bromine, which is weighed for this purpose in a small glass globe closed before the blowpipe after filling. The mean of several determinations showed that 1 c.c. of the solution contains 0·004884 grm. arsenious acid, a quantity corresponding 0·0125055 iodine. Four atoms of iodine correspond to two atoms of thallium, *i.e.*, 506·16 grms. iodine = 407·2 grms. thallium. Hence 1 c.c. of arsenious acid = 0·0100605 grm. thallium. The solution of iodine was obtained by diluting an approximately decinormal solution of iodine, carefully standardised with arsenious acid, so that 5 c.c. of the iodine solution exactly correspond to 1 c.c. of the arsenious acid. In order to carry out the method it is preferable to dissolve the substance as thallic sulphate. In case of any other thallic salt at least so much sulphuric acid must be added as would be required for the formation of thallic sulphate. This is absolutely necessary in case of thallic chloride, bromide, or iodide. If the corresponding thallous compounds are present after introducing the sulphuric acid bromine-water is added until the liquid has a distinct yellow colour, and it is then boiled until all free bromine is expelled and the liquid is colourless. If the compound is insoluble in water the insoluble thallous salts can be readily converted by bromine into soluble thallic salts. If, after the expulsion of the bromine, there appears a turbidity from the separation of thallium hydroxide a few drops of sulphuric acid are added. An excess of potassium iodide is added in the cold, the free acid is neutralised with sodium hydrocarbonate, an excess of which is added, and so much of the arsenical solution is dropped in with the burette as corresponds to the highest proportion of thallium in the substance. At first there is no change of colour, but in a short time the liquid begins to turn to a lighter colour. The decomposition is hastened by frequent agitation. If a few c.c. of arsenious acid have been added in excess the transformation is more rapid. In a quarter of an hour at furthest the precipitate is a pure yellow. As in titrating back this precipitate hinders the exact detection of the final reaction, it is best to conduct the operation in a measuring-flask, filling up to the mark as soon as the precipitate has assumed a pure yellow colour, mixing the liquid and filtering through a folded filter into a dry beaker. An aliquot portion is then titrated back with solution of iodine and starch. The liquid must on no account be filtered off until the precipitate is of a pure yellow colour. The method is, of course, not applicable if metals are present which react with arsenious acid, either becoming reduced or forming insoluble arsenites. Such metals may be previously removed by means of sodium hydrocarbonate. The author has applied the same method to the analysis of mercurial compounds, but the results obtained did not agree very closely.

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THE CHEMICAL NEWS.

Vol. LX. No. 1552.

ON THE NATURE OF THE REACTION BETWEEN SOLUTIONS OF FERRIC CHLORIDE AND POTASSIUM IODIDE, AND THE VOLUMETRIC TITRATION OF IRON IN THE FERRIC STATE.

By D. J. CARNEGIE, M.A.

In standard text-books* the reaction between solutions of ferric chloride and potassium iodide is formulated as follows:—

$$FeCl_3+KI=FeCl_2+KCl+I \quad . \quad . \quad . \quad (I.)$$

In many of the original papers on this reaction the same idea as to its mechanism prevails; witness, for example, the following sentence from a paper by Braun:—"und die Eigenschaft des Eisenchlorids durch Kalium Iodid in Eisenchlorür reducirt zu werden."

Duflos was the first to point out the applicability of the action between KI and $FeCl_3$ to the ready determination of iron in the ferric condition; translated into modern notation his original representation of the reaction appears as—

$$FeCl_3+3KI=FeI_2+I+3KCl \quad . \quad . \quad . \quad (II.)$$

In both these equations the ratio Fe : I is the same, but in the former the iron after the reaction exists as ferrous chloride, whereas the latter represents the residual iron as existing in the form of ferrous iodide. In short, in equation I., KI figures as a *direct reducing agent*—a *rôle* with which this substance is not generally credited.

Now it seems to me that the second equation is the more probable; it may conveniently be split up into two stages, one stage representing a double decomposition, the other a dissociation—

$$FeCl_3+3KI=FeI_3\dagger+3KCl.$$
$$FeI_3=FeI_2+I.$$

Duflos's method, modified in several of its details by Mohr, Braun, Spreng, and others, exists to-day as one of the standard methods for the estimation of iron, and the *modus* is described in all text-books, the representation of the fundamental action given being equation I. and not equation II. On several occasions I myself, and others working with me, have employed the method as described with very indifferent results. Reference to the original papers on the subject showed them to be vague and conflicting with respect to the best amount of KI to use, the necessity of nearly neutralising the iron solution, &c. These facts, coupled with the *à priori* improbability of KI acting as a direct reducing agent, induced me to re-investigate the action with a view to determining the conditions of its applicability as a volumetric method, and its true, as distinguished from its merely empirical, nature.

It is a well-known fact that when acidified solutions of KI are allowed to stand in contact with the air free iodine soon makes its appearance. This decompositon, *cæteris paribus*, takes place more readily the higher the temperature. So far as I know, this reaction has not been studied with respect to its bearing on iodometric processes. Some preliminary experiments on this point seemed therefore advisable. The accompanying table, which is sufficiently self-explicit, exhibits the results of these experiments. I do not claim absolute, but merely relative, accuracy for the results.

<1 signifies that one drop of the thiosulphate solution used (12 grms. per litre) was more than sufficient to react with the free iodine.

The KI used was free from iodate, and the solution contained 60 grms. per litre.

The dilute HClAq contained 0·1339 grms. HCl per c.c.

The ferrous iodide solution was made by allowing 2·27 grms. iodine to react with excess of *ferrum redactum* in 50 c.c. water. Thus 10 c.c. of the resulting solution contained 0·1 grm. Fe. The solution was allowed to stand in contact with the iron, and was drawn off as required by a "reverse filter."

It appears, therefore, that digestions involving acidified solutions of KI should always be carried out in an inert atmosphere of CO_2. This is an important point, which, I think, is not mentioned in English handbooks. The presence of this inert atmosphere is not of so much importance when distillation is used instead of digestion, provided that in the distillation the heating be rapid and the boiling-point soon reached. The form of distilling apparatus used will be mentioned later on. A somewhat curious fact in this connection is that acids will liberate iodine from fairly strong and hot solutions of KI, *even in an inert atmosphere*. Thus in experiment 7 the iodine which makes its appearance on heating, soon distils off and leaves a colourless liquid in the distilling flask; if now the distillation be long-continued till the residue becomes concentrated, the latter again shows the presence of free iodine, which, on account of the increased concentration of the KIAq it is impossible to boil off. This observation is not founded solely on experiment 7, which is merely an example from other similar experiments.

* See Sutton's "Volumetric Analysis," Fresenius's "Quantitative Analysis," Thorpe's "Quantitative Analysis," &c.

† I have before shown (*Proc. Chem. Soc.*, No. 61, 1888—1889) that fairly strong solutions of cupric iodide—currently regarded as non-existent—can be obtained. These solutions are very unstable, and behave just as dilute solutions of free iodine.

Table I.

	C.c. KI solution.	C.c. FeI_2 solution.	C.c. HClAq.	C.c. H_2O.	Digestion. Drops Thiosulph.	Digestion. Remarks.	Distillation (see further on). Drops Thiosulph.	Distillation (see further on). Remarks.
1.	5	—	—	15	0	¼ hour at 60°.		
2.	5	—	1	14	1	,, ,,	0	
3.	5	—	5	10	3	,, ,,	<1	
4.	5	—	5	10	11	½ hour at 60°.		
5.	5	—	1	14	8	¼ hour at 60°, then allowed to stand 2¾ hrs.		
6.	5	—	5	10	22			
7.	15	—	5	—	15	¼ hour at 60°.	2	The residue became colourless, then on further concentration again became coloured.
8.	5	—	5	10	<1	¼ hour at 60°, but in atmosphere of CO_2.		
9.	15	—	5	—	<1	,, ,,		
10.	5	5	5	5	4	¼ hour at 60°.		
11.	—	5	5	10	2	,, ,,		
12.	—	10	5	5	3	,, ,,	<1	

The measurement of the thiosulphate solution was effected by an easily improvised "stillimeter," on the principle of Mariotte's bottle; it consisted of a *small* glass lime tower (as used in preparation of NH_3) fitted with tubes as represented in the diagram. The efflux tube, *b*, consists of a quill tube drawn fine at its extremity and bent three times at right-angles, as figured. A tube of this kind, whose point of efflux is above the level *d*, works more satisfactorily than efflux tubes not fulfilling this condition. The size of the drop as well as the drop-rate is a function of the height *a d*; the size of the drop is also independent of the effective aperture of the tube *g*, *i.e.*, is independent of the precise opening of the tap, T.

The accuracy of such an apparatus is attested by the the following numbers, which show the weight of 30 drop portions delivered under varying conditions :—

1st Series, showing Dependence of Drop-weight on Level of *a*.

(α) Low level of *a*. ..	11·086 11·087 11·086 11·087
(β) Higher level of *a*..	11·118 11·1185 11·1185 11·118

2nd Series, showing that Drop-weight is Independent of Effective Aperture of Tube *g*.

(α) Tap T *fully* open..	11·0935 11·094
(β) Tap T *just* open ..	11·094 11·094

Using such an apparatus and very dilute standard solutions for the completion of any reaction, volumetric analyses may apparently be carried do a very high degree of accuracy. If the apparatus be used with a dilute solution for thus merely *completing* a reaction, its delivery should be tested against the stronger solution (used in the burette) every time the apparatus is filled.

It would seem almost impossible to obtain constant drops from a burette; we can never ensure that the tap is always opened to the same extent, and further, the effective pressure is always diminishing. The inconstancy of the following numbers (for the weight of 30 drops), obtained with one of Geissler's burettes, contrasts strongly with the constancy observed in the above experiments.

11·6325	burette full.
11·5840 11·5380 11·6020 11·6030 11·5960	burette about half full.
11·598 11·626	burette nearly empty.

It occurred to me that a choice between the two equations I. and II. might be made by investigating the actual amount of KI necessary to completely decompose a given mass of $FeCl_3$ under conditions admitting of a "complete" change. A ferric chloride solution was made in the ordinary way by solution of piano wire in HCl and subsequent oxidation of the solution with chlorine. After boiling off the excess of chlorine the acidity of the solution was *diminished* by the addition of KOHAq, and the *still fairly acid* solution made up to known volume. It was held more exact to determine the strength of the solution gravimetrically by precipitation with NH_3Aq than by primarily weighing accurately the iron dissolved. The mean of two closely agreeing experiments gave the strength as 0·0999 grm. per 10 c.c. A standard solution of KI (dried at 150°) was so made that 5 c.c. of the iron solution required 10 c.c. of the iodide solution in order to satisfy the ratio Fe : KI.

The first set of experiments was made in the ordinary way with digestion-bottles. In all cases but the last F, the air in the bottle was displaced by a rapid stream of CO_2 before digestion.* The temperature of the bath employed was 60° C., and the duration of digestion twenty minutes in each case.

Table II.

	Ratio $\frac{\text{molecules KI}}{\text{atoms Fe}}$.	C.c. thiosulphate used to react with liberated iodine.
A	1	14·2
B	2	17·9
C	3	18·35
D	3½	18·6
E	Very large but unmeasured	18·7
F	,,	19·55

The numbers given in the first three cases marked the first disappearance of the blue iodide of starch; on allowing the solutions to stand the phenomenon of "after blueing" (*nachblauung*) was observed. By alternately adding enough thiosulphate to destroy the slight blue colour and allowing to stand on the water-bath for some time a point was reached after which no after-blueing was observed. This limit was always reached after a sum total of 18·6 to 18·7 c c. thiosulphate had been added.

The conclusions to be drawn from these experiments is that the reaction between $FeCl_3Aq$ and KIAq is complete only when rather over three molecules KI have been used for each atom of iron.† This fact speaks strongly in favour of equation II. The reason why exactly three molecules KI fail to completely decompose one molecule $FeCl_3$ is not far to seek. Under the conditions of the experiment there is no removal from the sphere of action, and the change is on that account an "incomplete" one, *i.e.*, factors and products are alike represented in the final equilibrium. When an excess of one of the factors of the change is taken the reaction is rendered complete so far as the other factor is concerned. In this case we see that the excess of KI above the ratio 3KI : Fe necessary to completely decompose the ferric chloride is small.

It occurred to me that by experimenting under conditions admitting the removal of the volatile iodine from the sphere of action I should find that *exactly* three molecules KI would completely decompose one molecule $FeCl_3$. In this I was mistaken. The distilling apparatus used in the following experiments was made completely of glass as figured. This form of apparatus offers many advantages over those usually described. When occasion demands the delivery tube, which is ground to fit the flask, can be rapidly and easily disconnected without any fear of a back-flow from R. The shaded portions, *a a*, represent bindings of thick string to facilitate this disconnection. Moreover, this form of delivery-tube is very easily washed out. Special experiment showed that with this apparatus, and using in R 10 c.c. of a solution of KI containing 40 grms. per litre, the whole of the iodine librated in *a* was retained by R. It is best to support the flask on an asbestos card, in the middle of which a small hole is cut. The flask can thus be rapidly heated by a bare flame without fear of fracture (see discussion of Table I.)

The experimental results are appended in Table III.

The results of these experiments (in which it is to be noted that the KI used to absorb the iodine was not measured in each case) are very irregular, and, on the whole, lead to the conclusion that in distillation one molecule KI serves to completely decompose one mole-

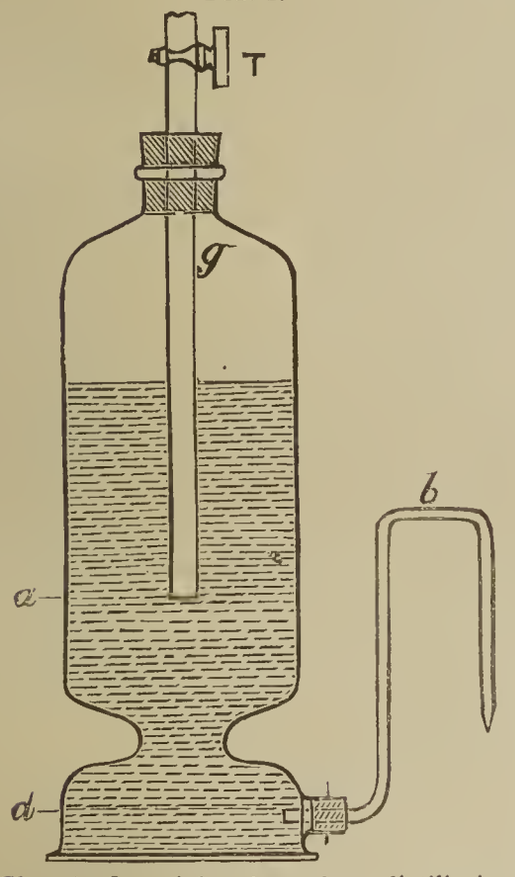
* I find, on reference to Mohr's "Titrirmethode," that he recommends the addition of a few lumps of acid carbonate of sodium to the digestion-bottle before heating. Experience, however, has taught me to favour extrinsically generated CO_2

† Braun (*Zeit. f. An. Chem.*, 1864, iii, p. 453) regards 0·5 to 1 grm. KI sufficient for 1 grm. Fe in the form of ferric chloride; from the above experiments it appears that each grm. Fe requires about 3·5 grms. KI.

Table III.

	Ratio $\frac{\text{molecules KI}}{\text{atoms Fe}}$.	C.c. thiosulphate required.	Remarks.
A ..	Just over 1.	14·9	In all these cases the residues in *a* were quite colourless. The values here given are in each case means of somewhat irregular results.
B ..	2	15·55	
C ..	3	14·6	
D ..	3½	14·45	
E ..	Very large but unmeasured.	—	The residue in A in this case did not become iodine-free, even on re-distilling twice with excess of water.

Fig. 1.



cule $FeCl_3$. At first sight, then, these distillation experiments would seem to support equation I., but I will show later on that they are by no means incompatible with the more rational equation II., supported in its turn by eqn. I.

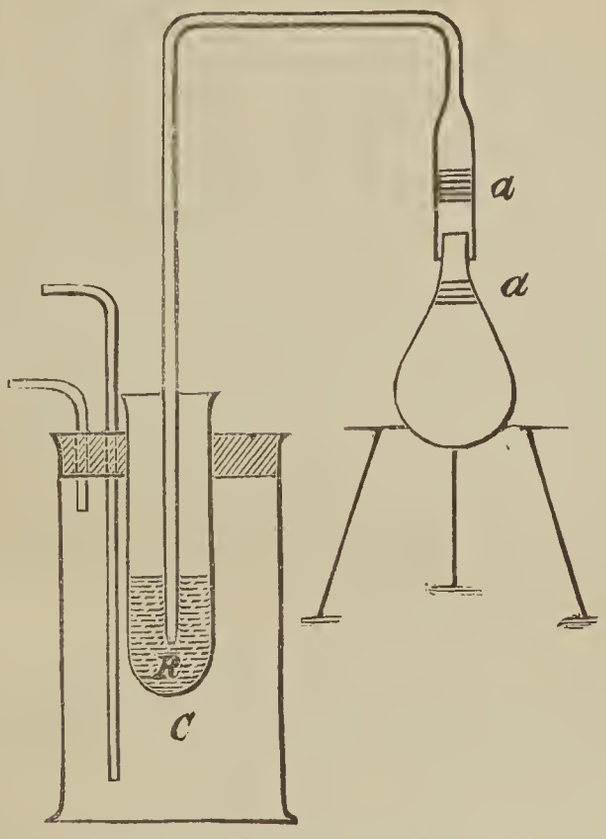
The mean of these results gives 14·7 c.c. thiosulphate as marking the limit of the action; whereas the digestion method gave 18.7 c.c. thiosulphate for the same limit. The thiosulphate was now standardised in the ordinary way against pure iodine, and it was found that (1) 16·3, (2)16·4 c.c. was the quantity theoretically necessary for the iodine liberated from KI by 5 c.c. of the $FeCl_3Aq$, the quantity always used in these experiments.

I subsequently found that the cause of these discrepancies was the presence of an impurity in the "puriss." potassium iodide used. It is well known that commercial KI frequently contains KOH and K_2CO_3; but this impurity is apparently not confined to the commercial article, for samples of the purest KI supplied by two of the best known British firms contained respectively 2·2 per cent and 1·9 per cent.* Now the extreme importance of this impurity in connection with iodometry in all its bearings has never, I think, been sufficiently emphasized; the text-books, in the fervour of their warnings with respect to the evils arising from the presence of iodate in potassium iodide, have completely overlooked quite as formidable an impurity. Both KOH and K_2CO_3 "fix" free iodine, and it therefore follows that all iodometric estimations (even the simple standardisation of thiosulphate against pure iodine dissolved in KI), unless special precautions have been taken to the contrary, are vitiated in varying degree by the alkalinity of the impure KI.

In the light of this revelation I now undertook a new series of experiments, with most satisfactory results, applying to the case in hand a fact worked out by Fresenius, viz.: that acid carbonates of the alkali metals have no action on iodine.

Fifty grms. KI were dissolved in 200 c.c. water, and the solution supersaturated with CO_2; 10 c.c. of the resulting solution were used to catch the liberated iodine in each of the following distillation experiments. A fresh

Fig. 2.



R, tube containing concentrated solution KI.
C, condensing apparatus.

thiosulphate solution was used in these later experiments; hence it became necessary to repeat the digestion-experiments, which otherwise would have been unnecessary, as the standard KI solution used was always thoroughly saturated with CO_2 (see *ante*).

Table IV

Distillation.

Ratio $\frac{\text{mols. KI}}{\text{atoms Fe}}$	C.c. thiosulphate sol.	Remarks.
1½	(α) 17·2 (β) 17·3 (γ) 17·3	
3	(α) 17·3 (β) 17·3	
Very large, but unmeasured.	17·3	In this case the residue never became iodine-free; consequently the residue and distillate were mixed and titrated together.

* A sample of Schuchardt's pot. iodatum puriss. was obtained and was found to contain only the *merest trace* of free alkali.

In all these cases the measured amount of the standard KI solution was first introduced into the distilling flask, then CO_2 passed through to saturation, and finally the iron solution was added. I am firmly convinced that the distillation method is much more rapid and workable than the digestion method.

TABLE V.

Digestion.

Ratio $\frac{\text{mols. KI}}{\text{atoms Fe}}$	C.c. thiosulphate used.	Remarks.
$1\frac{1}{2}$	17·25	
$4\frac{1}{2}$	17·4	
Very large, but unmeasured	17·3	In this case the colour of iodide of starch first disappeared at 15·8 c.c. thio.; then the phenomenon of *nach blauung* presented itself till the thio. titre reached the limit 17·3.

A direct determination of the iodine-titre of the thiosulphate solution (using the carbonated KIAq for the solution of the iodine) gave 1 c.c. thio. =0·00655 grms. iodine. Of such a solution theory demands 17·26 c.c. for the iodine liberated by the amount of iron contained in 5 c.c. of the $FeCl_3Aq$ used. As is seen the theoretical demand is well satisfied by the experimental result.

The necessity of titrating the thiosulphate solution in kind (*i.e.*, against a ferric chloride solution of known strength), has always been urged in the papers on Duflos's reaction; but by giving heed to the precautions here indicated such a procedure is unnecessary. In short, the reaction between $FeCl_3Aq$ and KIAq is removed from the category of those "chemical equations which, though right enough as such, are only *approximately correct* as theories of the processes of titration."

The fact that the ratio* KI : Fe suffices for a complete reaction by the distillation method does not in the least incline me to favour equation I. as a representation of the *modus* of the change. I would explain what takes place, in terms of equation II., as follows:—

$$FeCl_3 + KI = (\alpha)\ \tfrac{1}{3}FeI_3 + KCl + \tfrac{2}{3}FeCl_3.$$

The $\frac{1}{3}$ FeI_3 at the high temperature of the experiment is completely resolved into $\frac{1}{3}$ FeI_2 + $\frac{1}{3}$ I, which latter is removed from sphere of action, rendering stage (α) complete. The second stage in the equation may therefore be represented:—

$$(\beta)\ \tfrac{1}{3}FeI_2 + KCl + \tfrac{2}{3}FeCl_3 + \tfrac{1}{3}I$$

Now, in a previous paper I have shown that solutions of $FeCl_3$ behave towards certain other substances practically as if they contained free chlorine. Re-arranging β in accordance with this view we get—

$$(\gamma)\ \tfrac{1}{3}FeI_2 + KCl + \tfrac{2}{3}FeCl_2 + \tfrac{1}{3}Cl_2 + \tfrac{1}{3}I.$$

This loose chlorine of the ferric salt now decomposes the ferrous iodide as follows:—

$$(\delta)\ \tfrac{1}{3}FeCl_2 + \tfrac{1}{3}I_2 + KCl + \tfrac{2}{3}FeCl_2 + \tfrac{1}{3}I$$

or, re-arranging,—

$$(\varepsilon)\ FeCl_2 + I + KCl.$$

It appears, therefore, that the final composition of the residue in this particular case is identical with that demanded by equation I., but that this final state is arrived at through the primary operation of Duflos's equation II.

* The fact that apparently rather more than 1 molecule KI per molecule $FeCl_3$ was required for completion of the change (*vide* Table III. A) is to be ascribed to the presence of impurity (K_2O) in the iodide weighed to make the standard solution used in this set of experiments. Experiments with KI freed from alkali by Grove's method showed that under these conditions 1 molecule KI serves to completely decompose 1 molecule $FeCl_3$.

The various stages when the ratio 2KI : Fe is employed may be similarly represented.

$$FeCl_3 + 2KI = (\alpha)\ \tfrac{2}{3}FeI_3 + 2KCl + \tfrac{1}{3}FeCl_3$$
$$(\beta)\quad \overbrace{\tfrac{2}{3}FeI_2} + \tfrac{2}{3}I + 2KCl + \overbrace{\tfrac{1}{3}FeCl_3}$$
$$(\gamma)\ \overbrace{\tfrac{1}{2}FeI_2 + \tfrac{1}{6}FeI_2} + \tfrac{2}{3}I + 2KCl + \overbrace{\tfrac{1}{6}Cl_2 + \tfrac{1}{3}FeCl_2}$$
$$(\delta)\ \tfrac{1}{2}FeI_2 + \tfrac{1}{6}FeCl_2 + \tfrac{2}{3}I + 2KCl + \tfrac{1}{6}I_2 + \tfrac{1}{3}FeCl_2$$

or, re-arranging,—

$$(\varepsilon)\ \tfrac{1}{2}FeI_2 + \tfrac{1}{2}FeCl_2 + I + 2KCl.$$

When the ratio nKI : Fe is used, where n = or >3, the equation is as follows:—

$$FeCl_3 + n KI = FeI_3 + 3KCl + (n-3)KI$$
$$= FeI_2 + I + 3KCl + (n-3)KI.$$

It is obvious that in order to substantiate these views dilute solutions of $FeCl_3$ should have the power of reacting with dilute solutions of FeI_2, and such is the case.

A mixture of 5 c.c. FeI_2Aq (containing about 0·1 grm. Fe) with 30 c.c. water, and 5 c.c. of the standard $FeCl_3$ solution showed the presence of much free iodine, even in the cold, and in an inert atmosphere of CO_2.

A mixture of 1·7 c.c. FeI_2Aq, 3·4 c.c. $FeCl_3Aq$, and 35 c.c. water, corresponding to stage β of the equation representing the reaction with the ratio KI : Fe, behaved similarly.

In the light of these facts the cause of the "after-bluing" in the digestion experiments, which *only* appeared when less than about $3\frac{1}{2}$ molecules KI per molecule $FeCl_3$ was used, is apparent. An equilibrium exists between $FeCl_2Aq$, FeI_2Aq, IAq (FeI_3Aq), $FeCl_3Aq$, and KIAq. On adding thiosulphate to decolouration this equilibrium is destroyed by the change of free iodine into sodium iodide. Slowly at low temperatures, more quickly at high ones, the NaI formed, reinforcing the small residual amount of KI, decomposes some of the residual $FeCl_3$, forming a new equilibrium, which in turn is again similarly affected by a fresh addition of thiosulphate, and so on till no more $FeCl_3$ remains unchanged. This "after-bluing" can, in accordance with the above explanation, be readily imitated by adding thiosulphate slowly to $FeCl_3Aq$ containing a little iodine and starch solution. Under these conditions we get the blue colour of iodide of starch coming and going just as in the above experiments.

This paper would be incomplete without an expression of the thanks I owe to Mr. Pattison Muir, in whose laboratory the work detailed was carried out, and to whose kind help I am a large debtor.

Gonville and Caius College Laboratory,
Cambridge.

A NEW PROCESS FOR THE VOLUMETRIC DETERMINATION OF SILVER, MERCURY, AND THALLIUM BY MEANS OF POTASSIUM IODIDE.

By ADOLPHE CARNOT

CHEMISTS possess excellent volumetric methods for the determination of silver, and also some, much less accurate, for the estimation of mercury. The author proposes a new method applicable to both these metals with almost equal correctness. It is founded upon the insolubility of silver and mercury iodides in a nitric solution, provided that such solution contains no alkaline iodide. The potassium iodide employed as a reagent is poured little by little into the acid solution until the starch used as an indicator is coloured by the iodine. The liberation of the iodine is due to the presence of a very strong proportion of nitric acid, in preference such as contain nitrous products, like that which has been exposed for some time to the light in a bottle. The silver or mercury iodide may be collected and weighed, but it is preferable to

use the reagent as a standard solution, and to measure the volume of liquid necessary for precipitation.

I. First take the case of mercury, which must be in the mercuric state. The solution diluted with water to 100 or 150 c.c. is put in a beaker with about 10 c.c. of nitric acid and a little clear starch paste. Then a decinormal solution of potassium iodide (16·61 grms. of the pure salt per litre) is dropped in from a burette, stirring continually with a glass rod. Each drop produces at first a yellow precipitate, which quickly dissolves on stirring; then the precipitate turns gradually to red. At the moment when the mercury is entirely converted into the insoluble iodide the least excess of the reagent liberates iodine, which at once colours the starch.

Before the end of the operation we perceive, at the place where the drops of the reagent fall, blue and afterwards brown spots, which disappear at first rapidly, then they form trains of a dark brown in the midst of the red liquid, and finally give it a general brownish tint. The exact moment must be seized when a permanent change of colour is observed. If this is ever so little overstepped, the liquid, when left to itself, remains of a blue colour after the subsidence of the red precipitate.

When the quantity of mercury to be determined has been approximately found by a first operation, it is advantageous to add at once almost the total quantity of the reagent necessary, and to add the starch and the nitric acid afterwards. The remainder of the standard reagent is then added drop by drop until the reaction is completed.

Synthetic experiments on quantities of mercury varying from 0·002 grm. and 0·100 grm. have given results as satisfactory as possible, leaving uncertainty only as to the tenths of a m.grm. The method is not suitable in presence of free hydrochloric acid or of alkaline chlorides, conditions which must be kept in mind in preparing the solution to be operated upon.

II. Silver is determined in the same manner as mercury. If the substance in question is of unknown composition we make first an approximate determination.

According to this first datum we calculate the approximate weight of the silver contained in the portion taken for analysis, we dissolve it in nitric acid, dilute it to 100 c.c., introduce the calculated quantity of the decinormal potassium iodide, and stir briskly so as to collect the pale yellow precipitate of silver iodide in the form of dense clots. We decant the liquid along with a little washing-water into a beaker, add some c.c. of starch paste, and about 10 c.c. of nitric acid slightly nitrous. If at this moment the liquid becomes blue it is exactly decolourised by means of a centinormal solution of silver nitrate (1·7 grms. nitrate per litre). If it is not coloured blue we pour in at first potassium iodide until the permanent blue tint appears, which is then removed again by means of the centinormal silver solution.

In this manner the author has obtained results accurate to 0·1 or 0·2 m.grm. when operating upon known quantities of silver, from 1 to 200 m.grms.

This process, in certain points, resembles that of Pisani, described in the *Annales des Mines*, founded upon the decolouration of silver nitrate by starch iodide prepared in advance in a standard solution. But the potassium iodide employed does not give rise, like Pisani's free iodine process, to the formation of silver hypoiodite, a cause of uncertainty in the volumetric determination of silver if the metal is in rather large quantities.

III. Thallium, which forms in a nitric solution a yellow iodide a little less insoluble than those of silver and mercury, may be determined by the same method, though with a little less accuracy.

Palladium gives rise to similar reactions, but its iodide is of so deep a colour that it is not possible to seize the exact moment when the free iodine begins to colour the starch. The process is, therefore, not applicable to its determination by this method.—*Comptes Rendus* (cix., p. 177).

NOTE ON THE

ANALYSIS OF CONCENTRATED SUPERPHOSPHATE.

By JOHN HUGHES, F.C.S., F.I.C.

Concentrated superphosphate containing from 37 to 41 per cent of phosphoric acid soluble in water usually contains in addition from 4 to 5 per cent of phosphoric acid, which is combined with oxide of iron and alumina in the form of precipitated phosphate.

This precipitated or reduced phosphate, correctly speaking, is *not soluble* in water, but is *soluble* in a concentrated solution of the superphosphate. Therefore, in extracting the ordinary soluble phosphoric acid in such superphosphates, or indeed in any superphosphate made from materials containing much iron and alumina, it is most important to take care that sufficient water is added for the *first extraction*, otherwise the soluble phosphoric acid is returned 1 to 2 per cent too high. In other words, the less water used for the *first* extraction the higher the percentage of soluble phosphoric acid reported.

The following two experiments are sufficient to demonstrate the practical importance of attention to the quantity of water employed:—

	No. 1.	No. 2
Percentage of phosphoric anhydride ..	37·95	39·60
Equal to tribasic phosphate of lime rendered soluble by acid	82·85	86·44

In No. 1 experiment 1½ grms. of superphosphate were placed in a small beaker and a little water added to soften the mass and allow of breaking up all lumps, the volume of the solution being then increased with cold water to 90 c.c., allowed to stand five minutes, and then the supernatant liquor filtered off. To the residue another 90 c.c. of cold water was then added, the whole carefully stirred, allowed to settle, and filtered as before. Finally the residue, with about 60 c.c. of water, was warmed gently, and the whole brought upon the filter and washed once with hot water.

In the filtrate the soluble phosphoric anhydride was determined by the magnesia method with the usual precautions.

In No. 2 experiment 3 grms. of superphosphate were taken and the mass broken up as in No. 1, but only 30 c.c. of cold water added for the first extraction. After standing, the clear liquid was filtered off and another 30 c.c. of water added for second extraction, then 60 c.c. for third, and 90 c.c. for fourth extraction, the residue being finally warmed up with boiling water and brought on the filter as in the case of No. 1, the total volume of liquid being the same in each experiment. In No. 2, as the the third and fourth washings came into the filtrate, the precipitate of phosphate of iron and alumina became apparent as the filtrate became diluted, whereas in No. 1 (which represents the process employed by the writer in all analyses of superphosphate) this precipitate is formed in the original solution and is collected on the filter with other insoluble phosphates.

It will be seen from the above results that, by omitting to take the precaution of adding sufficient water to the first extraction, phosphoric acid equal to 3½ of ordinary soluble phosphate of lime passes into the filtrate in the form of phosphate of iron and alumina, and becomes included with the phosphoric acid *soluble* in water, whereas it really exists in a form *insoluble* in pure water.

At the present time, when a considerable quantity of this concentrated superphosphate is being purchased and numerous analyses are being made, the author believes it will be useful to point out the probable cause of the differences between the analytical results of duplicate samples of this quality of superphosphate.

Analytical Laboratory,
79, Mark Lane, E.C., Aug. 12 1889.

ON PRECIOUS STONES.*

By GEORGE F. KUNZ.

(Continued from p. 84).

Imports of Diamonds.—From the Custom import lists we find that after deducting the approximate value of cut stones other than the diamond, we find that import duty was paid on about 90,000,000 dollars worth of cut diamonds in the last twenty-one years; of these 68,000,000 dollars worth were imported during the last ten years. In 1868 1,000,000 dollars worth were imported, and 1,200,000 dollars worth in 1867, but about 10,000,000 dollars worth in 1887, or ten times as many as twenty years ago, showing the increase of wealth and the great popularity of the diamond among Americans, the above being the wholesale import figures. A single firm sells more than the entire imports of twenty years ago.

Diamond dust worth 464,905 dollars has been imported since 1878, 289,430 dollars worth from 1868 to 1878, and in 1869 to 1871 only 228 dollars worth; whereas with the opening of the Kimberley mines 80,707 dollars worth were imported the first year, showing what great benefit the arts received from the opening of the African diamond mines.

In 1878 the importations of uncut diamonds amounted to 63,270 dollars; in 1887 to 262,357 dollars; the total for the decade was 2,728,214 dollars, while in 1883 there were imported 443,996 dollars worth, showing that although we are cutting four times as many diamonds as we were in 1878, yet the importations have been falling off. This is partly because in the years from 1882 to 1885 a number of our jewellers opened diamond cutting establishments, but have either given up the business or sold out to others; for, in spite of the protective duty of 10 per cent on cut stones, cutting cannot be profitably carried on here on a scale large enough to enable one of the partners to reside in London, the great market for rough diamonds, to take advantage of every fluctuation in the market, and purchase large parcels which can be cut immediately and converted into cash; for nothing is bought and sold on a closer margin than rough diamonds.

Diamond Cutting.—The recent death of Mr. Henry D. Morse, of Boston, known as the pioneer diamond cutter of the United States, brings to mind many interesting reminiscences. He has scarcely received the credit he deserved for his work. That he was the first in this country to cut diamonds is well known, and the best cutters in the United States to-day received their training under him. But educating young Americans, both men and women, to his art, was not his greatest work. He showed the world that the art which had so long been monopolised by the Hollanders, was degenerating in their hands into a mere mechanical trade. His treatment of the diamond has given a great stimulus to the industry both in the United States and abroad. Shops were opened here and in London in consequence of his success. He was one of the few who studied the diamond scientifically, and he taught his pupils that mathematical precision in cutting greatly enhances the beauty and consequently the value of the gem. His artistic eye, sound judgment, and keen perception enabled him to carry the art nearer to perfection than is often attained.

It was in his shop that a machine for cutting diamonds was invented which did away in great measure with the tediousness and inaccuracy of the old manual process. Thanks to his labours, we now have among us the best cutters in the world—men who can treat the diamond as it should be treated to develop its greatest beauty. The fact that so many fine stones were re-cut here after he started his wheel led to a great improvement abroad in cutting, especially in the French Jura, and in Switzerland, where both sexes are now employed at the trade; and, as a result, the diamonds sold to-day are decidedly better than those of twenty years ago, before Mr. Morse turned his attention to the work. He, above all others, has shown us that diamond cutting is properly an art and not an industry.

There are at present about 12 cutting establishments in this country, employing from 1 to 50 men each, and in all about 100, at salaries ranging from 20 to 50 dollars per week. Most of the cutting done here is of a high class, some shops being almost entirely employed in re-cutting stones previously cut abroad. Ten years ago nearly all the diamonds used in the United States were purchased through brokers or importers. To-day, owing to the marvellous growth of the diamond business here, and the facilities for transatlantic travel, many of the large retail houses buy their diamonds direct in the European markets; and some have even established branches or agencies abroad.

In 1877 an international syndicate, composed of London, Paris, and Amsterdam jewellers, wishing to establish a uniform value for the carat, confirmed 205 m.grms. as the standard, and this has been pretty generally used abroad. Recently the discussion of the question has been re-opened, and it will probably end in the general adoption of the above standard in place of the twenty or thirty conflicting systems now in use in different parts of the world.

Twenty years ago the wholesale diamond merchants of Amsterdam did not exceed eight in number; but the development of the African mines has given so great an impetus to the trade, that within the past decade several diamond exchanges, or clubs, have been established as head-quarters for the transaction of business; one of these, the "Handelsbond," has a membership of 800 and owns a fine building, the rooms of which are so arranged with respect to light as to render deception difficult and to facilitate the sale of diamonds. Others, known as the "Golconda," and the "Koh-i-noor," are generally thronged with brokers and merchants, as also are the neighbouring coffee houses.

At present there are between 50 and 60 large diamond polishing establishments, employing perhaps 3500 polishers, who, however, no longer receive the princely wages of from 80 to 200 dollars per week which they received when the African mines first began to produce so largely, and much higher prices were paid for products of the second and third quality. When fortune smiled on them the cutters lived in luxury; to-day they only receive 15 to 40 dollars a week, and some even less than the former figure. To day every establishment does its own selling. It will doubtless be eventually a question of the survival of the fittest, and the entire cutting will be controlled by a few powerful firms.

Sapphire.—In 1882 a very remarkable discovery of sapphire was made in the Zanskar range of the north-western Cashmere Himalaya, near the line of perpetual snow, a short distance from the villege of Machel, and one-half day's journey from the top of Umasi Pass. The stones were found at the foot of a precipice, where a land-slide had taken place, the including rocks being gneiss and mica.

At first they were merely collected by the villagers, who were attracted by the beautiful colours; and so little was their value realised that they were used as flints for striking fire with steel. They were so abundant at first that one writer speaks of having seen about a hundred-weight of them in the possession of a single native. Traders, however, soon carried them to the distant commercial centres, where their value became known. There was an instant rush of jewellers' agents to the locality of the mine, and the price rose rapidly until about £20 per ounce was paid for good specimens, at which rate they have remained. The Maharajah of Cashmere promptly exercised his authority and sent a regiment of sepoys to take possession of the mines and harry the natives who were suspected of having stones in their possession or any knowledge of new localities where the

* Abstract from "Mineral Resources of the United States."

gems could be found. Any one they laid hands on who had money was suspected either of having sold sapphires or being about to purchase them, and was despoiled, or even imprisoned. This naturally enough had the effect of compelling secrecy. Several crystals were found weighing from 100 to 300 carats each. During the first year of the discovery the Delhi jewellers are said to have bought up more than £20,000 worth of these sapphires. Exceptionally fine sapphires to-day bring from 65 dols. per carat to 125 dols., which is less than before this great find.

The acquisition of the Burmese ruby mines cost the British Government a vast sum of money. On the wars of 1826 and 1852 England expended 75,000,000 dollars and 15,000,000 dollars, respectively, and after all this sacrifice of treasure the Burmah and Bombay Trading Company claimed, four years ago, that King Thebaw, of Burmah, had arbitrarily cancelled the leases by which the company controlled the output of the ruby mines near Mandalay. A meeting was accordingly held at Rangoon, on October 11, 1884, presided over by Mr. J. Thompson, agent for Messrs. Gillanders, Arbuthnot, and Co. The result was the war of 1886, which involved the raising of an army of 30,000 men and an outlay of 5,000,000 dollars, but the British Government gained control of the long coveted ruby mines. The question which next presented itself was, how should they be worked? Several firms were desirous of securing the lease, and after the Indian Government had virtually closed a lease to Messrs. Streeter and Co., the London jewellers, at an annual rental of 4 lakhs of rupees (£40,000), for a term of five and one-half years, with the privilege of collecting 30 per cent on all stones mined by others, the Home Government revoked the lease for some unexplained reason, probably on account of trade jealousies, although Mr. Streeter had apparently every assurance of the acceptance of his proposition, and had even made preparations to begin work at the mines.

The ruby mines of Burmah are situated in the valley of the Mogok, 51 miles from the bank of the Irrawaddy river, and about 75 miles north of Mandalay, at an altitude of 4200 feet. Concerning these mines very little has been learned up to the present, as they were always the monopoly of the Crown and were jealously guarded. It was said that they paid King Theebaw's Government annually 100,000 rupees, and one year 150,000 rupees. Mining is carried on there by forty or fifty wealthy natives, who employ the poorer townspeople at liberal wages; but at present only seventy-eight mines or diggings are in operation, and the work is done in the most primitive manner. The gravel is carried in baskets. The holes from which they are taken are allowed to fill with water every night. All of the gems are sent to Ruby Hall, Mandalay, to be valued. At present the royalty exacted by the English Government is 30 per cent. A stone was lately sold in Mandalay for 8000 rupees, but without the knowledge of the officials.

One thing, at least, we learned from the British occupation of Burmah, namely, that King Thebaw did not own the dishes of rubies which were said to outrival anything known. His possessions of this kind proved to be only a few stones of poor quality.

(To be continued).

Fuel and its Applications.—Messrs. J. and A. Churchill hope to publish in September an important work on "Fuel and its Applications," by Mr. E. J. Mills, F.R.S., and Mr. F. J. Rowan. It will be the first volume of a large work on Chemical Technology, of which Mr. C. E. Groves, F.R.S., will be the general editor, and which will be founded on one written by Richardson and Ronalds, familiarly known as "Knapp's Technology." Messrs. Mills and Rowan's work on Fuel is in reality a new work, in which the applications of fuel to arts and manufactures, as introduced by the most modern discoveries, is given to the scientific world. The volume will be profusely illustrated.

A RAPID METHOD FOR THE REDUCTION OF FERRIC SULPHATE IN VOLUMETRIC ANALYSIS.*

By CLEMENS JONES, Hokendauqua, Pa.,
Chemist to the Thomas Iron Company.

The difficulties attending the reduction of ferric sulphate in the determination of metallic iron by the method of Marguerite are often serious, and affect time, patience, and accuracy. They depend upon the condition and purity of the zinc used, the state of saturation of the solution, acidity, and temperature.

D. J. Carnegie (Chem. News, lvii., No. 1481) says that ferric solutions are instaneously reduced by the use of zinc-dust. But there are obvious objections to its employment in quantitative work. Dr. Drown found that "a concentrated solution, not too acid, was reduced by five grms. of pulverised zinc in two or three minutes, without other heating than that due to the chemical action." But the zinc in excess of the stoichiometrical amount must be dissolved. This has been the main obstacle. Large excess of sulphuric acid, heat, or both, must then be employed; and either involves loss of both time and accuracy in the volumetric method.

Marguerite's method is, in point of celerity and refinement, the most scientific of all the "iron methods." If the iron solutions have been properly prepared the end-reaction is sharper and more quickly obtained than by any other. There is no loss in testing for final oxidation, as potassic permanganate is its own indicator. Besides, the permanganate solution can be most quickly prepared and accurately standardised.

Hence there is a natural preference for this method in determining metallic iron. It permits direct and rapid titration. Only facilitate the reduction of the ferric sulphate, and it is the most valuable of all methods, combining the utmost rapidity with the highest accuracy attainable.

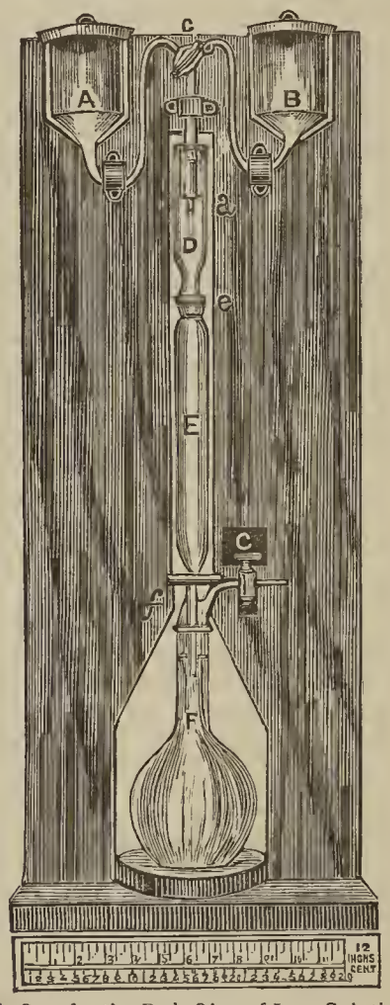
There is no difficulty in obtaining iron as ferric sulphate; but the reduction of this to the ferrous state has hindered the precision of the permanganate method. Discrepancies in results are all to be set down to the errors introduced in the reduction with zinc. The care to secure complete reduction—how frequently is it lost through the presence of a minute grain of zinc, washed down from the neck of a flask in titrating, and now derisively tossing up a little chain of hydrogen bubbles! Again, a very hot solution will decompose an excess of reagent. And, moreover, as I shall again remark, it is probable that the largest impurity in pulverised zinc is not iron, as heretofore supposed, but carbon.

The size of the particles of the pulverised zinc employed in the method which this paper describes is determined by passing through a 40-mesh upon a 60-mesh sieve.

Observing the action on zinc of ferric solution in sulphuric acid, I noticed that in all cases, with practically the same amount of acid and zinc, the latter dissolved more rapidly when the solution was more highly saturated with ferric salt; that the time for reduction, under the conditions mentioned, was dependent on the strength of the ferric solution. This was evidence that a sufficient number of zinc particles should be exposed in a proper ratio to the ferric salt; that each molecule takes the same time to reduce when unaffected by its unreduced neighbour, which is the time of contact; and that, therefore, were each molecule presented to new particles of zinc successively, reduction would be instantaneous. Filtering the ferric solution through pulverised zinc would then demonstrate this fact, which I found to be the case. *A solution of ferric sulphate is instaneously and completely reduced by filtering through pulverised zinc.*

* Read before the American Inst. Mining Engineers, New York Meeting, Feb., 1889.

The apparatus figured below was designed for the rapid reduction of ferric solutions. It consists of two cups,* A and B, of about 300 c.c. capacity, the outlets of which connect alternately, by means of a 3-way cock, C, into the joint-tube, D. This tube is provided with a packing space, *d*, which is filled with an asbestos roll kept in place by a ring of cork. The tube moves up and down freely. At its lower end *e*, it is ground to fit the detachable tube, E. This is for the pulverised zinc, and at its lower end has a stopper, *f*, ground to fit the titrating flask, F, of about 700 c.c. capacity. The stop-cock, G, connects with the vacuum-pump. The tube E is disconnected by pushing it up, grasping the neck of the flask with one hand, removing with the other the round block which supports the flask, and then detaching the flask F. The tube E now rests on the little shelf shown in the cut. This is drawn out, and frees the tube at its ground-joint, *e*.



Reductor, for the Reduction of Iron Solution by Filtration through Zinc.

A wad of fine glass wool, sufficiently thick to make a good filter, is inserted into the tube, and the pulverised zinc is filled over this for four-fifths the length of the tube. This holds about 300 grms., which is enough for 60 filtrations. The tube is then replaced by reversing the manner of removal, connection is made with the filter-pump, and the apparatus is ready for use. It is first necessary to wash the column of zinc with dilute sulphuric acid. This acid is made up of one part of acid of 1·84 sp. gr. to two parts of distilled water, and is used throughout in all work upon iron determinations. Of this about 30 c.c. is taken, transferred to the cup A, and diluted to 300 c.c. Stop-cock G is opened for suction, and then the three-way cock C is turned to discharge the cup A. A vacuum of 5 to 6 pounds or more, gauge-indication, must be used, since the large volume of disengaged hydrogen retards the filtration. The cup and the column of zinc are then washed free from acid by five rinsings. This operation is repeated four times, and is then finished for this tubeful of zinc.

Below is a series of trials, undertaken to determine the proper correction for iron in the zinc. Owing to the small amount of reagent required for the end-reaction, it was impossible to obtain a reading under 0·1 c.c., which, as will be seen further on, is too much for even so large a quantity of zinc.

No. of test.	Amount of $K_2Mn_2O_8$. C.c.
1	0·4
2	0·2
3	0·13
4	0·12
1	0·4
2	0·2
3	0·15
4	0·13
1	0·4
2	0·15
3	0·13
4	0·11
1	0·4
2	0·2
3	0·13
4	0·1

These were made at different times upon new quantities of zinc, and with solutions of $K_2Mn_2O_8$ of slightly varying strength. Beyond the fourth trial in each case it was impossible to get less than one drop of the reagent into the solution. This is nearly 0·1 c.c., and in every instance gave a strong colouration.*

Evidently the largest amount of iron in the zinc is only on the outside of the particles, as the quantity dissolved in the reductor is less than five grms. for each filtration. By the ordinary method of dissolving all the zinc, the correction is rarely below 0·15 c.c. for 5 grms.

Exactly the same procedure is adopted to reduce a ferric sulphate solution, except to use both cups A and B. After the first is emptied it is washed with cold water five times. This incidentally cools the column of zinc and retards unnecessary solution. The other cup is then connected by turning the 3-way cock C, and washed in like manner. In each case this suffices to free the apparatus from all traces of iron or sulphuric acid. G is then closed, the 3-way cock is turned again to relieve the pressure, and the flask is removed. Time for reduction, two minutes.

Solutions obtained in this way are beautifully clear and perfectly reduced. The volume and temperature are practically constant: the former being about 400 c.c., and the latter about 40° centigrade. Uniformity marks the entire process, and there is a minimum quantity of zinc sulphate. Dilute solutions must be used. There should be not over 50 c.c. sulphuric acid in 300 c.c. of the ferric solution ready for reduction.

An experiment was tried in reducing the solutions after oxidation, used in standardising the permanganate. Iron wire taken at 0·996 Fe.

Standardisation.

	Weight of wire. Grm.	$K_2Mn_2O_8$ C.c.	Reaction.	Factor.
No. 1.	0·1271	16·48	Tinged	1 c.c. = 0·007681 Fe
No. 2.	0·12175	15·78	Sharp	1 c.c. = 0·007684 Fe

Reduction of these Solutions.

	Reduction.	$K_2Mn_2O_8$. C.c.	Reaction.
No. 1	Complete	16·42	Tinged
No. 2	,,	15·8	Sharp

* I find this form of cup not so convenient as the bulb-shape of a separatory funnel of the same capacity.

* I have since obtained a reading down to 0·03 c.c. by closing the burette-tip.

This treatment applied to a hæmatite ore gave (No. 2969)—

	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$. C.c.	Reaction.	Iron. Per cent.
No. 1.	0·1527	Complete	7·2	Tinged	34·7207
No. 2.	0·1526	,,	7·2	Sharp	34·7441
(Reverted: filtered through the Reductor)—					
No. 1		,,	7·2	Sharp	
No. 2		,,	7·2	,,	

Direct determination of metallic iron in the wire used in standardising gave the following results:—Weight of wire, 0·12405 grm. dissolved in sulphuric acid and oxidised. Reduced by filtration.

Reduction.	$K_2Mn_2O_8$ c.c.	Reaction.	Iron. Per cent.
Complete	16·07	Sharp	99·5420

Factor, 1 c.c. $K_2Mn_2O_8$=0·007684 Fe.

Solution again reduced by filtration. Reduction complete. $K_2Mn_2O_8$, 16·10 c.c., as compared with 16·07 in the former reduction. Difference, 0·03.

The *apparent* correction for iron in the zinc is the increase in last reading or 0·03 c.c. of the reagent. Time required to reduce and titrate this solution twice, *ten minutes*.

While the apparent correction is thus 0·03 c.c., it is inadvisable to use it as a constant, since the true correction can be applied for each case, and is really variable, depending upon acidity and degree of saturation.

In the following example, the test of hæmatite ore (No. 2922), carried through in duplicate, the ferric sulphate was first reduced by the usual method of adding the zinc to the solution, and then entirely dissolving it, and deducting 0·3 c.c. as the correction after titration. Each solution was then filtered through the Reductor, and on the supposition that for each treatment with zinc (on account of filtration) but 0·1 c.c. is to be deducted; the results are seen to be coincident. By "Reverted" is meant filtering through the Reductor. The value of 1 c.c. $K_2Mn_2O_8$ is 0·007678 Fe.

	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$.	Correction.	Iron. P.c.
No. 1	0·1360	Complete	7·4 sharp.	0·3=7·1	40·06
,,	Reverted	,,	7·3 ,,	0·2=7·1	=40·06
No. 2	0·1379	,,	7·49 ,,	0·3=7·19	=40·03
,,	Reverted	,,	7·39 ,,	0·2=7·19	=40·03

Another (No. 2971), with a difficulty-fusible residue, was tried directly, each solution being reduced twice by filtration. Time for reducing and titrating in duplicate, twenty minutes.

	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$. C.c.	Reaction.	Iron. Per cent.
No. 1	0·1505	Complete	9·27	Sharp	
2nd trial		,,	9·21	,,	=47·0230
No. 2	0·1823	,,	11·29	,,	
2nd trial		,,	11·23	,,	=46·9132

Assuming that for ordinary purposes the correction obtained by reverting the solution used to standardise the permanganate would be a safe one, I have applied it to the determination of iron in an ore, with the following results:—

Standardisation.

	Weight of wire. Grm.	$K_2Mn_2O_8$. C.c.	Reduction.	Correction. C.c.
No. 1.	0·11915	15·48		
	Reverted	15·55	Complete	0·07
No. 2.	0·1261	16·4		
,,	Reverted	16·44	,,	0·04

Factor, 1 c.c. $K_2Mn_2O_8$=0·007664 e.

Determination.

No. 2997)	Weight of ore, grm.	$K_2Mn_2O_8$. C.c.	Correction.		Iron. Per cent.
No. 1.	0·1576	9·58	0·07	9·51	46·246
No. 2.	0·2351	14·3	0·07	14·23	46·388

In like manner a rich hæmatite ore (No. 3066) gave:—

No.	Weight of ore. Grm.	Metallic iron. Per cent.
1.	0·2302	60·03
2.	0·1645	60·17

Theoretically a neutral, or nearly neutral, solution of ferric sulphate should be reduced by zinc in this way without dissolving the latter appreciably, at least, not to the extent of introducing the error due to its impurity. As nearly satisfying these conditions, by the use of a minimum of sulphuric acid, the two following examples afford a remarkable demonstration. The experiments were conducted like the foregoing:—

Factor 1 c.c. $K_2Mn_2O_8$=0·007656 Fe.

No. 1.

Weight of wire, 0·12085 grm.	Amount of $K_2Mn_2O_8$, c.c.
1st trial	15·72
2nd ,, ...	15·78

No. 2.

Weight of wire, 0·11315 grm.	$K_2Mn_2O_8$, c.c.
1st trial	14·695
2nd ,, ...	14·695

Metallic iron 99·432 per cent.

There appears to be a deeply-rooted belief that iron is the only impurity in pulverised zinc which reduces the $K_2Mn_2O_8$; but I think the error is in all cases largely due to the carbonaceous residue. Five grms. of zinc were dissolved in sulphuric acid, and then found to require 0·13 c.c. of $K_2Mn_2O_8$. After oxidation, a test of the solution gave *no* colouration with potassium sulpho-cyanate. Oxidation with nitric acid gave a like result.

Twenty-five c.c. of sulphuric acid were diluted to 300 c.c. and passed through the reductor. $K_2Mn_2O_8$ required 0·05 c.c. One drop more was added, and the solution allowed to stand until clear. It was then tested with potassium sulpho-cyanate, and gave *no* colouration. A like experience followed in repeated trials of dissolving the zinc directly; but subsequent treatment of these solutions with ammonia and filtration gave evidence of iron. A determination of iron in the zinc used in these experiments gave the following:—5 grms. of zinc were dissolved in sulphuric acid. $K_2Mn_2O_8$ required 0·1 c.c.=0·0154 per cent iron. As in the first case, 5 grms. were dissolved and the solution filtered through the reductor. $K_2Mn_2O_8$ required 0·12 c.c. Increase, 0·02 c.c., equivalent to 0·0030 per cent iron.

Mr. P. W. Shimer has since suggested to me the probability of lead existing in the black residue. This I have found to be the case.

Ignition of the residue leaves a small fused mass which, on dissolving in hydrochloric acid, reveals iron by the sulpho-cyanate. May not this residue be soluble under accidental conditions when exposed to the action of the solution for an hour or more by the old method of reduction? I have frequently noticed that it is perceptibly smaller in bulk. Again, if the solution is warm, may not final oxidation of the ferrous salt have an effect in dissolving it?

If it should prove to be a carbon compound, the reducing action on the $K_2Mn_2O_8$ would be increased beyond the correction for iron as ordinarily obtained. Filtration undoubtedly obviates these difficulties.

As touching this reducing action, the following experience may be cited:—An analysis in duplicate by the old method gave an unaccountable difference in results. The one solution, with the high result, was noticed to have a

dark colour and lustre. Subsequently this proved to be due to a very finely divided sediment, apparently carbon.

(No. 2978)	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$. C.c.	Correction.	Iron. Per cent.
No. 1. ..	0·2174	Complete	11·75	0·3	40·47
No. 2. ..	0·1795	,,	11·12	0·3	46·31
No. 2. ..	Reverted	,,	9·61	0·15	40·49

Factor, 1 c.c. $K_2Mn_2O_8$=0·007684 Fe.

Here is another similar case:—

	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$. C.c.	Correction.	Iron. Per cent.
No. 1. ..	0·1951	Complete	16·95	0·18	65·80
No. 2. ..	0·1928	,,	15·6	0·18	60·92
No. 1. ..	Reverted	,,	15·9	0·3	61·21

Factor, 1 c.c. $K_2Mn_2O_8$=0·007656 Fe.

The following test of an ore is added as an illustration of the capability of this method for rapid reduction. 1 c.c.=0·007671 Fe.

	Weight of ore. Grm.	Reduction.	$K_2Mn_2O_8$. C.c.	Correction.	Iron. Per cent.
No. 1...	0·1566	Complete	13·35	0·05	65·1496
No. 2...	0·1820	,,	15·51	0·05	65·1569

Time required to reduce and titrate in duplicate, twenty minutes.

The investigation of this principle of reduction, which I believe to be new, has been governed by the time afforded in the few and brief intervals of regular technical work. I think the method capable of still further advancement and application. At the present stage of the enquiry, it presents the most rapid and accurate treatment for the estimation of iron.

The apparatus was made by Emil Greiner, 63, Maiden Lane, New York, whose intelligent and skilful workmanship has been of great service to me.

NOTICES OF BOOKS.

The Stevens Institute of Technology, Hoboken, New Jersey. Exterior and Interior Views by the Phototype Process, from Negatives by Prof. W. H. Bristol, M.E.

This work affords a two-fold interest. On the one hand, it gives us a brief view of the past history and the present condition of the Stevens Institute. On the other hand, it is important as illustrating the vast progress of photographic art.

The Stevens Institute owes its origin to private munificence. In 1867 the late Mr. E. A. Stevens bequeathed a suitable site and the sum of 150,000 dollars for the erection of a building "suitable for the uses of an institute of learning," and also, as an endowment for such institution, any sum, not exceeding 500,000 dollars, which his executors might think necessary. The executors considered the whole of this sum necessary, and appropriated it accordingly. But, on both sides of the Atlantic, there is many a slip between the cup and the lip. The Government of the United States demanded, and seized upon, 45,000 dols. as a "collateral inheritance tax," or, as we should say, legacy duty. Frequent attempts, we read, have been made to get this money returned, but without success—the more to be regretted as the Government of the United States seems to be suffering from a plethora of wealth. This transaction reminds us of the old evil days when Waterton, returning home with his splendid collections in natural history, a large part of which were destined for public institutions, found himself compelled to pay a tax of 20 per cent upon their supposed value.

In 1870 Prof. H. Morton, Ph.D., at that time occupying the Chair of Chemistry in the University of Pennsylvania, was appointed president, and a charter of incorporation was duly secured.

Chairs of physics, mathematics, chemistry, mechanical engineering, mechanical drawing, languages, and letters were at once instituted.

Chairs of experimental mechanics and shop-work, of marine engineering, of applied electricity, and of analytical chemistry have been subsequently added.

The photographs show the Front of the Institute Building, the East Side, the Institute Building looking east, the view through Castle Point Gateway, the rear of the Institute Buildings, the general views from the Institute looking eastwards and south-eastwards, the Gateway of Castle Point, Castle Point Homestead, the Old Lecture Hall, the Library, Physical Laboratory, the Engineering Lecture-room, the rooms for drawing looking eastwards, the Chemical Laboratory, the Work-shop looking north-eastwards, East Side of Work-shop, its West Side, the Foundry in Basement, the Mechanical Department in the East Basement, the Electrical Laboratory, the Electrical Lecture-room, the Electrical Gallery in Workshop, the Boat Engine of Colonel John Stevens (1804), the Stevens School, a preparatory institution, and the Entrance to the Stevens School. Some of these illustrations, as photographs, call for especial notice.

In the views of exteriors we notice that while the foregrounds are perfectly clear and distinct the distances have none of that heaviness so much complained of in photograph landscapes. This is particularly to be noticed in the view from the Institute looking to the east. Here the city and the open country in the back-ground gradually fade away in the distance, as in nature. In the view to the south-east the distance is also happily rendered. The view of the workshop looking north-eastwards shows a novel and ingenious method of overcoming a difficulty which may often present itself in photographing interiors. We find here a row of windows facing the observer, or the camera, whilst between them and the eye come in a multitude of dark objects, full of details, wheels, driving-bands, riggers, chains depending from pulleys, &c., yet there is no blurring or obscurity. This result is obtained, as President Morton informs us, by calling in the flash-light to the assistance of daylight. The windows were first covered with dark screens, and the camera was used with a small stop. Long exposures were given, and the "flash-light pistol" was used a number of times at the points which a previous negative had shown to be deficient in illumination. Then the lens was covered up, the screens were removed from the windows, and the camera was uncovered again for half a second. This useful expedient has been applied in some of the other interiors.

Some of the rooms are illuminated with glow-lamps, others with gas, and others seem to be fitted up for both these kinds of lighting.

Judging from these illustrations we should conclude that the Stevens Institute turns its attention much more to mechanical than to chemical technology. The chemical laboratory appears well organised for analysis and for research, but we see no workshops where the student may be initiated in the various branches of industrial chemistry. Perhaps if the Government of the United States sees its way to refund the 45,000 dollars this deficiency may be supplied.

Journal and Proceedings of the Royal Society of New South Wales. Sydney: The Society's House. London: Trübner and Co.

A paper on an "Improvement in Anemometers," by Mr. H. C. Russell, F.R.S., makes known the startling fact that the pressure of the wind in sudden gusts may amount to at least 95 lbs. per square foot. Australia is not, indeed, liable to the frequent tornados which inflict such damage

in the United States, but a gentleman who took part in the discussion on Mr. Russell's paper mentions a storm coming up from the southward which twisted the head off a gigantic tree, from three to four feet in diameter, the head, which must have weighed 200 tons, being suspended in the air before it fell to the ground.

A paper by J. H. Maiden, F.L.S., on "Indigenous Australian Forage Plants," enumerates a number of poisonous plants which occasion at times much damage to cattle. Some of the principles which they contain would form interesting subjects for chemical research.

A much dreaded plant is *Bulbine bulbosa*, the "Native Onion," a liliaceous plant, which is found in all the colonies except Western Australia. It proves fatal to sheep, horses, and cattle.

Castanospermum australe, the "Moreton Bay chesnut," or bogum of the aborigines, is found in Queensland and the northern portion of New South Wales. It is accused of destroying cattle, though the seeds when cooked are quite harmless to man.

Eumophila longifolia, the emu-bush, is remarkable as one of the first trees to be barked by rabbits.

Euphorbia Drummondi is almost invariably fatal to sheep. The head swells to an enormous extent, and becomes so heavy that the animal drags it along the ground.

Gastrolobium spp. are familiary known as poison bushes and render some tracts of country unoccupiable.

Swainsonia Greyana causes madness in horses. After eating it they "obstinately refuse to cross a small twig lying on the ground, imagining it to be a great log." Sometimes they endeavour to climb trees and commit other absurdities." Some alkaloid is probably present.

Mr. J. H. Maiden also contributes an important paper on Australian products containing tannin. Numbers of these materials contain proportions of tannin sufficient for use on the spot, *i.e.*, 13 to 14 per cent. A few are sufficient to be worth exportation, *e.g.*, *Acacia decuriens*, 36 per cent; *A. elata*, 20 per cent.; *Eugenia Smithii*, 28 per cent.

Considering the large production of hides in the colonies he considers it probable that the leather industries have a great future in Australia.

Prof. A. Liversedge, F.R.S., read a paper on "Some New South Wales Minerals." The "platinum" nodules found along the coast contain only about 30 per cent of platinum, and are made up chiefly of osmium and iridium.

Medals and money prizes are offered by the Society for the best original papers on—

The influence of the Australian climate in the development and modification of disease.

On the silver-ore deposits of New South Wales.

On the occurrence of precious stones in New South Wales, with a description of the deposits.

The papers must be sent in not later than May 1st, 1890.

The subjects for the succeeding year, to be sent in not later than May 1st, 1891, are—

The meteorology of Australia, New Zealand, and Tasmania.

The anatomy and life-history of the *Echidna* and the *Platypus*.

The microscopic structure of Australian rocks.

It must be noticed that no award will be made for a mere compilation. A memoir, to be successful, must be, in part at least, the result of original work on the part of the sender.

Analysis of Lead Peroxide.—L. Opificius.—The author dissolves lead peroxide or red lead by covering the sample with nitric acid of sp. gr. 1·2, and adding a slip of chemically pure metallic copper. Without the application of heat the lead peroxide is quickly dissolved if frequently stirred. The process has the advantage of dispensing with the use of organic reducing agents.—*Chemiker Zeitung*.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 6, August 5, 1889.

Combination-heat of Fluorine and Hydrogen.—MM. Berthelot and Moissan.—When gaseous fluorine and hydrogen combine, forming gaseous hydrofluoric acid, the heat evolved = 37·6 cals. If the hydrofluoric acid is in solution the heat = 49·4 cals.

The Relations of Atmospheric Nitrogen with Arable Mould.—Th. Schlœsing.—The author mentions that Hellriegel and Wilfarth have proved that leguminous plants really fix gaseous nitrogen, requiring, however, the co-operation of certain microbia inhabiting vegetable mould. These organisms fix themselves on the rootlets, producing the tubercles well known to botanists. M. Schlœsing has, therefore, repeated his experiments to ascertain if the bare soil is capable of fixing nitrogen. The results have been constantly negative, not one sample being found which, when bare of vegetation, fixes gaseous nitrogen. Hence he concludes that such earths, if they exist, are exceptions upon which the farmer cannot reckon.

Study of the Electric Phenomena Produced by Solar Radiations.—Albert Nodon.—Solar radiations, if they encounter an insulated conductor (metal or carbon) communicate to it a positive charge. The magnitude of this charge increases with the intensity of the solar radiations, and decreases with the hygrometric state of the air. The phenomenon ceases if clouds pass before the sun. Solar radiations may be one of the causes of the electrisation of clouds.

Researches on the Sulphites.—P. J. Hartog.—The author has studied, chiefly from a thermo-chemical point of view, the normal double potassium and ammonium sulphite and the sodium-potassium sulphite-bisulphite.

The Combustion-heat of Some Organic Compounds.—J. Ossipoff.—A thermo-chemical study of the bisubstituted succinic acids.

Chemical and Thermic Study of the Phenolsulphuric Acids. Orthophenolsulphuric Acid.—S. Allain Le Canu.—The author lets fall, drop by drop, pure refrigerated sulphuric acid into pure phenol, kept at −10°, stirring, and letting the mixture slowly take the ordinary temperature, and keeping the vessel covered in order to exclude the moisture of the air. In about eight days all the phenol is dissolved and the mixture is poured slowly into water, avoiding any rise of temperature. The sulphuric acid remaining free is determined and got rid of by neutralising with barium carbonate. The barium sulphate is filtered off and the filtrate is neutralised with pure potassium hydrocarbonate.

On Camphor Monochlorised by Means of Hypochlorous Acid.—P. Cazeneuve.—This camphor is not chlorised in the methyl or propyl chains. Its slow decomposition by alcoholic potassa and the production of a chloro-nitro-derivative by the action of fuming nitric acid do not allow it to be considered as comparable to benzyl chloride.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 3.

Wave-length of Spectral Lines of Metals in the Ultra-violet Portion of the Spectrum.—J. Trowbridge and W. C. Sabine (*Proceedings of American Academy of Science and Art*, per Chemical News).

Researches on Phenomena of Depression in Thermometers.—Memoirs have appeared by R. Weber, H. F. Wiebe, and A. Böttcher. The first-mentioned shows that the presence of alumina in the glass has in this respect no injurious influence.

General Law of Decrease of Volume during the Solution of Salts in Water.—A. Hentzsch (*Annalen der Physik und Chemie*).—No details are given.

Catalytic Action of Metals upon Detonating Gas and the Occlusion of Hydrogen.—A. Berliner.—The author regards occluded hydrogen as the cause of all the catalytic phenomena which he has observed (*Annalen der Physik*). Stephen Cooke has studied the reductive action of hydrogen in presence of platinum (*Glasgow Phil. Trans.*, per Chemical News).

Ultra-violet Spectral Lines of Nickel and Cobalt. — G. D. Liveing and J. Dewar.— *Proceedings Royal Society.*

Influence of Temperature upon Evaporation and Diffusion of Vapours.—A. Winkelmann (*Annalen der Physik und Chemie*).—No particulars are given.

Measurement of Rate of Efflux of Liquids from Narrow Apertures.—Th. Vautier (*Annales de Chimie et Physique*).—No particulars are given.

Prevention of Bumping during Boiling.—C. Tomlinson (Chemical News).

Determination of Melting-point in Oils Containing Soap.—W. F. K. Stock.—From the *Analyst.*

Spectral Apparatus.—Hugo Krüss.—For particulars the reader is referred to the *Zeitschrift fur Instrumentenkunde.*

Microspectrometer.—Th. W. Engelmann.—For construction the reader is referred to the *Zeitschrift fur Instrumentenkunde.*

A New Microscopic Lamp.—W. Kochs and Max Wolz.—The nature of this lamp cannot be understood without the two accompanying figures.

A Substitute for the Oil-Spot in Bunsen's Photometer. — O. Lummer and E. Brodhun. — For the description of this apparatus the reader is referred to the original.

Polarising Apparatus.—Steeg and Reuter.—Improvements on Steeg's polarising apparatus for the examination of wines.

Apparatus for Measuring and Dropping Small Quantities of Mercury. — H. Wrampelmeyer. — An apparatus for always adding 0·05 c.c. of mercury in determinations of nitrogen by Wilfarth's modification of the Kjeldahl process.

New Gas-generating Apparatus. — Max Kæhler (*Chemiker Zeitung*).—This apparatus, for its description, requires the accompanying figure. J. H. J. Dagger (Chemical News) has proposed a gas apparatus on the same principle. P. M. Chantemille (*Bulletin de la Soc. Chimique*) has also devised an analogous apparatus. J. Martin, P. Hart, and G. Stillingfleet Johnson have proposed and constructed very similar appliances (Chemical News).

Determination of the Specific Gravity of Solids.—H. Unger proposes an instrument very similar to that previously described by Gisevius (*Pharmaceut. Zeitung*).

A Thermo-regulator for Temperatures between 40° and 60°.—E. Sehrwald (*Zeitschrift fur Wissensch. Microscopie*).—For the description we must refer to the original.

An Extraction Apparatus.—F. Schmidt and Haensch (*Chem. Centralblatt*).—The instrument agrees in principle with that proposed by C. M. King.

The Use of Hydrogen Peroxide for Analytical Purposes.—F. P. Dunnington (*Journal of Analytical Chemistry*).

An Evaporation-Stand. — A. Jolles (*Chemiker Zeitung*).—To which we refer for particulars.

A Washing-bottle for Ammonia.—F. M. Haldemann.—From the *Journal of Analytical Chemistry.*

Metallic Sponge as a Filtering Material.—O. E. Munroe (*Journal of Analytical Chemistry*).

Examination of Reagents as to Purity.—C. Krauch. —The author's instructions are not given.

Occurrence of Ferrous Oxide in Potassium Sulphocyanide. — J. Kranzfeld (*Pharm. Zeitung fur Russland*).—Already inserted.

Preparation of Non-fermentible Starch-paste for Iodometric Purposes.— G. Gastine (*Bulletin Soc. Chimique*).

Determination of Ferric Oxide and Alumina in Presence of Lime and Phosphoric Acid. — G. Kennepohl (*Chemiker Zeitung*).—The hydrochloric solution, placed in a 100 or 200 c.c. flask, is neutralised with ammonia; to the neutral or slightly ammoniacal solution there is further added, disregarding any precipitation produced by the ammonia, a slight excess of oxalic acid, and the whole is heated for some time to 80°. After the calcium oxalate has fully settled the flask is cooled, filled up to the mark, filtered though a folded filter, and a measured quantity of the filtrate is evaporated to dryness in a platinum capsule. The dry residue is slightly ignited to destroy the oxalic acid, the residue moistened with strong ammonia, dried in the covered capsule, and finally dissolved in strong hydrochloric acid with the aid of heat. The solution is washed into a flask and the iron-alumina phosphate is precipitated with ammonia and acetic acid and further treated in the usual manner.

Use of Aniline as Absorbent for Cyanogen in Gas-Analysis.—Morris Loeb.—From the *Journal of the Chemical Society.*

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Sugar Analysis —Could any of your readers give me the name and price of a good book on the refining and analysis of sugars, and the analysis of bone chars?—Greenock.

To Wholesale and Retail Chemists.

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MR. JAMES WHITTINDALE

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TO SELL BY AUCTION,

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THE CHEMICAL NEWS.

Vol. LX. No. 1553.

ON THE CAVENDISH EXPERIMENT.*

By C. V. BOYS, A.R.S.M., F.R.S.,
Assistant Professor of Physics at the Normal School of Science, South Kensington.

The Cavendish experiment for determining the constant of gravitation, from which the density of the earth may be calculated, is so well known that there is no occasion to describe it. This experiment, devised by the Rev. John Mitchell, F.R.S., was first carried out by Cavendish,† and has been since performed by Reich,‡ Baily,§ and Cornu and Baille,‖ who have all followed very closely the arrangement of Cavendish.

Owing to the very small value of the constant of gravitation, all these experimentalists have aimed at increasing the sensibility as much as possible. With this object a long beam, carrying at its ends considerable masses, has been suspended by a very long and very fine wire. The attracting masses have been made as large as possible, and they have been brought almost into contact with the sides of the long box in which the beam is suspended. Cornu, it is true, has reduced the dimensions of all the parts to about one-quarter of the original amount. His beam, an aluminium tube, is only half a metre long, and it carries at its ends masses of ¼ lb. each, instead of about 2 lbs. as used by Cavendish. This reduction of the dimensions to about one-quarter of those used previously is considered by Cornu to be one of the advantages of his apparatus, because, as he says, if the period of oscillation is unchanged, then the sensibility is independent of the mass of the suspended balls, and is inversely as the linear dimensions. I do not quite follow this, because, as I shall show, if all the dimensions are increased or diminished together the sensibility will be unchanged. If only the length of the beam is altered and the positions of the large attracting masses, so that they remain opposite to and the same distance from the ends of the beam, then the sensibility is inversely as the length.

The other improvements introduced by Cornu are the use of mercury for the attracting masses, which can be drawn from one pair of vessels to the other without coming near the apparatus, the use of a metal case connected with the earth to prevent electrical disturbances, and the electrical registration of the movements of the index on the scale, which was placed 560 c.m. from the mirror. The period of oscillation which has been used has varied between 398 seconds (Cornu) and 840 seconds (Cavendish). Cavendish found that with the very inconvenient period of 1800 seconds the balls knocked against the side of the case.

The difficulty that has been met with has been the perpetual shifting of the position of rest, due partly to the imperfect elasticity or fatigue of the torsion wires, and partly, as Cavendish proved experimentally, to the enormous effects of air currents set up by temperature differences in the box, which with large apparatus it is impossible to prevent. In every case the power of observing was in excess of the constancy of the effect actually produced. The observations of Cornu are the only ones which are comparable in accuracy with other physical measurements, and these, as far as the few figures given enable one to judge, show a very remarkable agreement between values obtained for the same thing from time to time.

Soon after I had made and found the value of quartz fibres for producing a very small and constant torsion, I thought that it might be possible to apply them to the Cavendish apparatus with advantage. Professor Tyndall, in a letter to a neighbour written some months ago, expressed the conviction that it would be possible to make a much smaller apparatus, in which the torsion should be produced by a quartz fibre. Last summer I began to prepare an instrument with a working beam 5 m.m. long, but other experimental work obliged me to put this on one side for a time. I have lately examined the theory of this instrument in some detail, and as I find that in many particulars there is an advantage in departing from the arrangement that has always been employed, I have lately prepared two pieces of apparatus, which, on trial, fully bear out the results of this inquiry.

I shall, therefore, first give a short account of the principles that should be followed in the design of the Cavendish apparatus, and then describe the results which I have obtained up to the present time.

As I have already stated, the sensibility of the apparatus is, if the period of oscillation is always the same, independent of the linear dimensions of the apparatus. Thus, if there are two instruments in which all the dimensions of one are n times the corresponding dimensions of the other, then the moment of inertia of the beam and its appendages will be as $n^5 : 1$, and, therefore, the torsion also must be as $n^5 : 1$. The attracting masses, both fixed and movable, will be as $n^3 : 1$, and their distance apart as $n : 1$. Therefore, the attraction will be as n^6/n^2 or $n^4 : 1$, and this is acting on an arm n times as long in the large instrument as in the small; therefore the moment will be as $n^5 : 1$, that is, in the same proportion as the torsion, and so the angle of deflection is unchanged.

If, however, the length of the beam only is changed, and the attracting masses are moved until they are opposite to and a fixed distance from the ends of the beam, then the moment of inertia will be altered in the ratio of $n^2 : 1$, while the corresponding moment will only change in the ratio of $n : 1$, and thus there is an advantage in reducing the length of the beam until one of two things happens, either it is difficult to find a sufficiently fine torsion thread that will safely carry the beam and produce the required period, and this, I believe, has up to the present time prevented the use of a beam less than half a metre in length, or else, when the length becomes nearly equal to the diameter of the attracting balls, they then act with such an increasing effect on the opposite suspended balls, so as to tend to deflect the beam in the opposite direction, that the balance of effect begins to fall short of that which would be due to the reduced dimensions if the opposite ball did not interfere.

* * * *

If the position which is chosen for each attracting mass is nearer the plane of the beam than the transverse plane, that is, if the azimuth of the large masses is less than 45°, the best length of the beam will be more than half that which would bring the ends opposite the attracting masses.

It might be urged against this argument that a difficulty would arise in finding a torsion fibre that would give to a very short beam loaded with balls that it will safely carry a period as great as five or ten minutes, and until quartz fibres existed there would have been a difficulty in using a beam much less than a foot long, but it is now possible to hang a thing only half an inch long and weighing from 20 to 30 grains by a fibre not more than a foot in length, so as to have a period of five minutes. If the moment of inertia of the heaviest beam of a certain length that a fibre will safely carry is so small that the period is too rapid, then the defect can be remedied by reducing the weight, for then a finer fibre can be used, and since the torsion varies approximately as the square

* Extracts from a Paper read before the Royal Society, June 20, 1889.
† *Phil. Trans.*, 1798, p. 469.
‡ *Comptes Rendus*, 1837, p. 697.
§ *Phil. Mag.*, vol. xxi., 1842, p. 111.
‖ *Comptes Rendus*, vol. lxxvi., p. 954; vol. lxxxvi., pp. 571, 699, 1001.

of the strength (not exactly because fine fibres carry heavier weights in proportion), the torsion will be reduced in a higher ratio, and so by making the suspended parts light enough, any slowness that may be required may be provided.

Practically, it is not convenient to use fibres much less than 1-10,000th of an inch in diameter, and these have a torsion ten thousand times less than that of ordinary spun glass. A fibre 1-5000th of an inch in diameter will carry a little over 30 grains.

Since with such small apparatus as I am now using it is easy to provide attracting masses which are very large in proportion to the length of the beam, while with large apparatus comparatively small masses must be made use of owing to the impossibility of dealing with balls of lead of great size, it is clear that much greater deflections can be produced with small than with large apparatus. For instance, to get the same effect in the same time from an instrument with a 6 foot beam that I get from one in which the beam is 5-8ths of an inch long, and the attracting balls are 2 inches in diameter, it would be necessary to provide and deal with a pair of balls each 25 feet in diameter and weighing 730 tons instead of about 1¾ lb. apiece. There is the further advantage in small apparatus that if for any reason the greatest possible effect is desired, attracting balls of gold would not be entirely unattainable, while such small masses as two piles of sovereigns could be used where qualitative effects only were to be shown. Owing to its strongly magnetic qualities, platinum is unsuited for experiments of this kind.

By far the greatest advantage that is met with in small apparatus is the perfect uniformity of temperature which is easily obtained; whereas, with apparatus of large size, this alone makes really accurate work next to impossible. The construction to which this inquiry has led me, and which will be described later, is especially suitable for maintaining a uniform temperature in that part of the instrument in which the beam and mirror are suspended.

With such small beams as I am now using it is much more convenient to replace the long thin box generally employed to protect the beam from disturbance by a vertical tube of circular section, in which the beam with its mirror can revolve freely. This has the further advantage that if the beam is hung centrally the attraction of the tube produces no effect, and the troublesome and approximate calculations which have been necessary to find the effect of the box are no longer required. The attracting weights, which must be outside the tube, must be made to take alternately positions on the two sides of the beam, so as to deflect it first in one direction and then in the other. For this purpose they are most conveniently fastened to the inside of a larger metal tube, which can be made to revolve on an axis coincident with the axis of the smaller tube. There are obviously two planes, one containing and one at right angles to the beam, in which the centres of the attracting balls will lie when they produce no deflection. At some intermediate position the deflection will be a maximum. Now it is a matter of some importance to choose this maximum position for the attracting masses, because, in showing the experiment to an audience, the largest effect should be obtained that the instrument is capable of producing; while in exact measures of the constant of gravitatation this position has the further advantage that the only measurement which there is any difficulty in making, viz., the angle between the line joining the large masses and the line joining the small, which may be called the azimuth of the instrument, becomes of little consequence under these circumstances. In the ordinary arrangement the slightest uncertainty in this angle will produce a relatively large uncertainty in the result. I have already stated that if an angle of 45° is chosen the distance between the centres of the large balls should be $2\sqrt{2}$ times the length of the beam, and the converse of course is true. As it would not be possible at this distance to employ attracting balls with a diameter much more than 1½ times the length of the beam, and as balls much larger than this are just as easily made and used, it will be well to find out what will be the position for maximum deflection when the centres of the attracting balls are any distance apart.

* * * *

If an attracting ball is placed in a position of maximum effect it will act on the further suspended ball, tending to deflect the beam in the opposite direction, and this will become more marked as the distance between the centres of the attracting balls increases, and so the increased effect which would be true to a greater attracting ball may be largely compensated by the increased action on the remote end of the beam. The azimuth at which the maximum effect is produced is also changed.

I have practically overcome this difficulty by arranging the two sides of the apparatus at different levels. Each large ball is at or near the same level as the neighbouring small ball, but one pair is removed from the level of the other by about the diameter of the large balls, which, in the apparatus which I have now the honour to submit to the Society, is nearly five times as great as the distance *in plan* between the two small balls.

In order to realise more fully the effect of a variety of arrangements I have, for my own satisfaction, calculated the values of the deflecting forces in an instrument in which the distance between the centres of the attracting balls is five times the length of the beam for every azimuth, and for differences of levels of 0, 1, 2, 3, 4, and 5 times the length of the beam.

(To be continued).

CONTRIBUTIONS TO THE CHEMISTRY OF STORAGE BATTERIES. No. 2.*

By E. FRANKLAND, D.C.L., F.R.S.

Under this title I communicated to the Royal Society, in February, 1883,† the results of some experiments on the reactions occurring during the charging and discharging of a storage cell. I showed that no appreciable part of the storage effect was due to occluded gases, as had been previously suggested by some chemists and physicists; but that the act of charging consisted essentially in the decomposition of lead sulphate, whilst the discharge was produced by the recomposition of this salt.

The establishment of these, as practically the only reactions going on in a storage cell, enabled me to prescribe a very simple method by which the charge in any cell could be ascertained, for as sulphuric acid is liberated during the charging and absorbed by the active material of the plates during discharge, the amount of charge could at any time be measured by ascertaining the amount of free sulphuric acid in the cell; in other words, by simply determining the specific gravity of the electrolyte; and this method has since been very generally adopted by the users of storage batteries.

In continuing these experiments it soon became evident that the lead sulphate formed and decomposed in the cell could not be the ordinary white sulphate hitherto known to chemists, because, in the first place, the active material of the plates always remains coloured even after discharge, and secondly, because whenever white sulphate is produced through abnormal reactions in the cell, it is afterwards decomposed only with extreme difficulty by the electric current.

In order to obtain some light upon the composition of the sulphate formed and decomposed in the cell, I have studied the action of dilute sulphuric acid upon litharge and minium.

* A Paper read before the Royal Society, June 20, 1889.

† *Proceedings of the Royal Society*, vol. xxxv., p. 67.

Action of Dilute Sulphuric Acid on Litharge.

Finely powdered litharge was treated with successive portions of dilute sulphuric acid until the liquid remains strongly acid after prolonged trituration. The resulting insoluble buff-coloured powder was washed with water till free from acid, and dried first at 100° C. and afterwards at 150—160°. The loss at this higher temperature was less than 0·2 per cent, and was therefore due to hygroscopic moisture.

PbO and SO_3 were then determined in the dried compound as follows :—The salt was dissolved in a small quantity of pure concentrated solution of caustic potash, and the solution, after dilution, was saturated with CO_2. (According to H. Rose, COPbo″ is soluble in $COKo_2$, but not in COHoKo). Any excess of CO_2, which might have caused the COPbo″ to dissolve, was avoided by warming the liquid with the precipitate on the water-bath to a temperature at which the COHoKo begins to dissociate. The liquid was then allowed to cool and stand twelve hours before filtering. The COPbo″ was filtered off, converted into nitrate, and precipitated and weighed as sulphate. The sulphuric acid was determined in the filtrate from the COPbo″.

1·2964 grms. of the salt gave 0·6647 grm. baric sulphate and 1·4437 grms. plumbic sulphate.

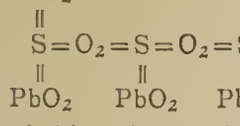
These numbers agree closely with the formula—

$$(SO_3)_3(PbO)_5,$$

as is seen from the following comparison of calculated and experimental numbers :—

	Calculated.		Found.
$3SO_3$	240	17·71	17·61
$5PbO$	1115	82·29	81·96
	1355	100·00	99·57

These analytical results suggest the following graphic formula :—



The formation of this salt may be represented by the following equation :—

$$5PbO + 3SO_4H_2 = S_3Pb_5O_{14} + 3OH_2.$$

Litharge. Sulphuric acid. Buff lead salt. Water.

Action of Dilute Sulphuric Acid on Minium.

Minium was treated with dilute sulphuric acid in exactly the same way as litharge, and the resulting brownish red compound dried first at 100° C. and afterwards at 150—160°. The loss at this higher temperature was again less than 0·2 per cent.

PbO, SO_3, and excess of oxygen were then determined in this salt in the following manner :—The salt was first treated with concentrated hydrochloric acid in order to reduce all the lead to the mon-oxide stage. The resulting mixture was then dissolved in caustic potash and treated as already described. The excess of oxygen was determined by finding the loss of weight which resulted from the evolution of CO_2 when the salt was treated with oxalic acid and dilute nitric acid.

2·1136 grms. of the salt gave 1·1978 grms. baric sulphate and 2·2710 grms. lead sulphate.

1·5110 grms. treated with oxalic acid and dilute nitric acid evolved 0·0910 grm. CO_2.

These numbers correspond to the following percentages :—

SO_3	19·45
PbO	79·03
O	1·09
	99·57

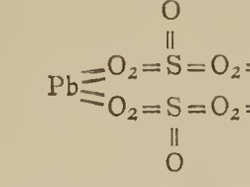
which agree with the formula—

$$S_2Pb_3O_{10},$$

as is seen from the following comparison :—

	Calculated.		Found.
S_2	64	7·57	7·78
Pb_3	621	73·49	73·36
O_{10}	160	18·94	18·43
	845	100·00	99·57

The composition of this salt may be represented graphically, thus—



The formation of this salt is expressed by the following equation :—

$$Pb_3O_4 + 2SO_4H_2 = S_2Pb_3O_{10} + 2OH_2.$$

Minium. Sulphuric acid. Red lead salt. Water.

These, then, are the salts which constitute the original active material of storage cells when that material is formed by the admixture of sulphuric acid with litharge or minium respectively, and it is highly probable that one or the other of these salts takes part in the electrolytic processes of the storage battery. It is fortunate that these hitherto unknown salts (and not the ordinary known sulphate) are formed in the cell reactions; for, in the alternative case, lead storage batteries would be practically valueless.

If the buff lead salt be the active material of the battery plates, then the following equations express the electrolytic reactions taking place in the cell :—

I. In charging—

(*a*). *Positive Plates.*

$$S_3Pb_5O_{14} + 3OH_2 + O_5 = 5PbO_2 + 3SO_4H_2.$$

Buff lead salt. Water.. Lead peroxide.* Sulphuric acid.

(*b*). *Negative Plates.*

$$S_3Pb_5O_{14} + 5H_2 = 5Pb + 3SO_4H_2 + 2OH_2.$$

II. In discharging—

(*a*). *Positive Plates.*

$$5PbO_2 + 3SO_4H_2 + 5H_2 = S_3Pb_5O_{14} + 8OH_2.$$

(*b*). *Negative Plates.*

$$5Pb + 3SO_4H_2 + O_5 = S_3Pb_5O_{14} + 3OH_2.$$

If the red lead salt be the active material, then the following equations express the same electrolytic reactions :—

I. In charging—

(*a*). *Positive Plates.*

$$S_2Pb_3O_{10} + O_2 + 2OH_2 = 3PbO_2 + 2SO_4H_2.$$

Red lead salt. Lead peroxide. Sulphuric acid.

(*b*). *Negative Plates.*

$$S_2Pb_3O_{10} + 4H_2O = 3Pb + 2SO_4H_2 + 2OH_2.$$

II. In discharging—

(*a*). *Positive Plates.*

$$3PbO_2 + 2SO_4H_2 + 2H_2 = S_2Pb_3O_{10} + 4OH_2.$$

(*b*). *Negative Plates.*

$$3Pb + 2SO_4H_2 + 2O_2 = S_2Pb_3O_{10} + 2OH_2.$$

An inspection of these equations discloses, in the case of the red lead salt, a fact which has already been roughly

* Mr, Fitzgerald considers that this peroxide is hydrated.

observed in practice, viz., that only half as much active material is electrolytically decomposed on the negative as on the positive plates; whence it follows that the weight of active material on the negative plates need not exceed one-half of that upon the positive plates; for, in the decomposition of the electrolyte, equivalent quantities of oxygen and hydrogen are evolved; that is to say, two atoms of hydrogen for each atom of oxygen. But in the decomposition of the red lead salt four times as many atoms of hydrogen are required to reduce the salt to metallic lead as atoms of oxygen which are necessary to transform the lead of the salt into peroxide. When, however, the active material of the positive plate has once been converted into peroxide of lead, it seems probable that the red salt only is formed; at all events, until the discharge at high potential is nearly completed, when there are indications of the production of the buff-coloured salt. But this is a point requiring further investigation.

I have to thank Dr. F. R. Japp, F.R.S., for his assistance in the analytical work of this investigation.

RAPID FILTRATION.

By REGINALD A. FESSENDEN,
Chemist, Edison Laboratory, Orange, N.J.

THE use of filter-pumps, as every chemist is aware, does not, in a very great number of cases, facilitate filtration: 1st, because a dense layer of the precipitate forms next the paper, which continually requires to be removed, and 2nd, if any considerable pressure is used particles of the precipitate will pass through.

FIG. 1.

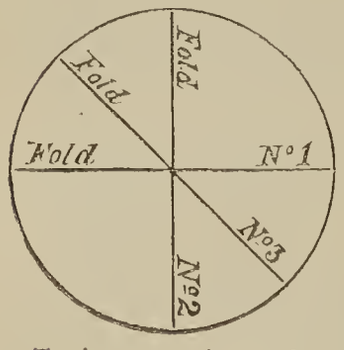
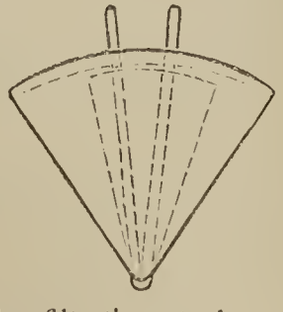


FIG. 2.

To increase the surface seems to be the better plan. Plaited filters partially effect this, but the precipitate cannot be easily detached from them, and they are troublesome to prepare. Ribbed funnels, while also an improvement, have only one side of the filter for use, the other side being covered with three thicknesses of filter-paper.

FIG. 3.

FIG. 4.

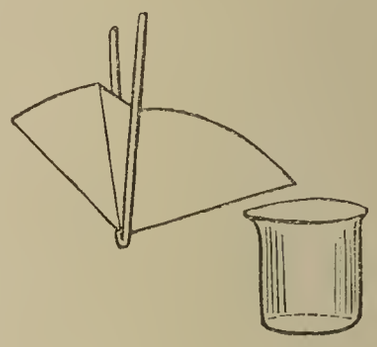


The following method enables filtrations to be made very rapidly, and in such a manner that the precipitate can be readily removed:—

The filter-paper is folded three times; folds Nos. 1 and 2 are towards the reader, No. 3 from him. The filter is then gathered (Fig. 2), and a piece of glass rod, bent at a very acute angle, inserted in the cleft of the filter (Figs. 3 and 4), thus giving a filtration surface of nearly four times the usual one.

The filtration being complete, the glass rod is grasped by the projecting ends and lifted from the funnel, bearing the filter upon it. One end of the filter-paper is then

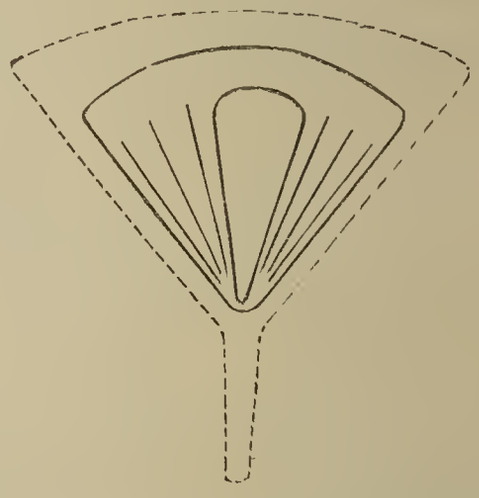
FIG. 5.



bent down, and the precipitate is easily washed off (Fig. 5).

An improvement on this is to use, instead of the glass rod, a plate of glass (Fig. 6) ribbed on both sides. This

FIG. 6.



renders the filtration very rapid indeed, and if it were made by the manufacturers of chemical apparatus, would no doubt be used.

From the Laboratory of
Thomas A. Edison.

ELECTROLYTIC SEPARATIONS.*

By EDGAR F. SMITH and LEE K. FRANKEL.

I. *Separation of Cadmium from Copper.*

THE results obtained in the electrolysis of cyanide solutions of mercury and copper, as well as the knowledge gained from our experiments in separating cadmium from zinc, induced us to try whether it would be possible to effect the separation of cadmium from copper in cyanide solution. The only electrolytic method proposed for the separation of these metals is that recommended by Smith (*Am. Chem. Journ.*, ii., 42), in which solutions containing a definite amount of free nitric acid were employed. We experienced no difficulty in making a complete separation after ascertaining the proper current strength. The conditions most favourable to the separation were essentially the same as those recorded in our former papers, viz., a dilution of 200 c.c., 5·5 grms. of potassium cyanide in each experiment, and a current generating 0·28 c.c. oxy-

* Read at the Meeting of the Chemical Section of the Franklin Institute, June 18, 1889.

hydrogen gas per minute. Time, sixteen to twenty hours. The results obtained were as follows:—

I.

Cadmium present.	Cu present.	Cadmium ound.
0·2426 grm.	50 per cent	0·2420

II.

Cadmium present.	Cu present.	Cadmium found.
0·2318 grm.	50 per cent	0·2331
	,,	0·2309
	,,	0·2315

III.

Cadmium present.	Cu present.	Cadmium found.
0·1024 grm.	100 per cent	0·1028
	,,	0·1019
	,,	0·1020
	,,	0·1032
	,,	0·1033
	,,	0·1034
	,,	0·1014

IV.

Cadmium present.	Cu present.	Cadmium found.
0·2046 grm.	100 per cent	0·2034

Copper was not found in any of the deposited cadmium, nor did we discover any of the latter metal in the filtrate containing the copper. The cadmium deposit invariably showed the grey colour characteristic of it.

II. *Action of the Current upon Metallic Sulphocyanides.*

It is well known that in the electrolysis of the sulphate or nitrate of manganese the oxide of this metal separates upon the positive pole. We have found that if an excess of potassium sulphocyanide be present no such deposition occurs, but, on the contrary, the metal itself will separate as a greyish white compact deposit upon the negative pole or the vessel attached to it. The addition of a sulphocyanide to the manganese solution undergoing electrolysis, after the oxide has already separated, will cause the solution of the latter. The current necessary for the deposition of metallic manganese, under the conditions mentioned above, should be feeble. The metallic deposit is inclined to rapidly oxidise, and whether manganese can be successfully determined in a quantitative way after this manner will depend very much upon whether we can prevent its oxidation during the drying process.

Nickel, cobalt, iron, and several other metals separate very rapidly from cold sulphocyanide solutions under the influence of a weak current.

Chemical Laboratory, Univ. of Pa.,
Philadelphia, June 18, 1889.

ON THE

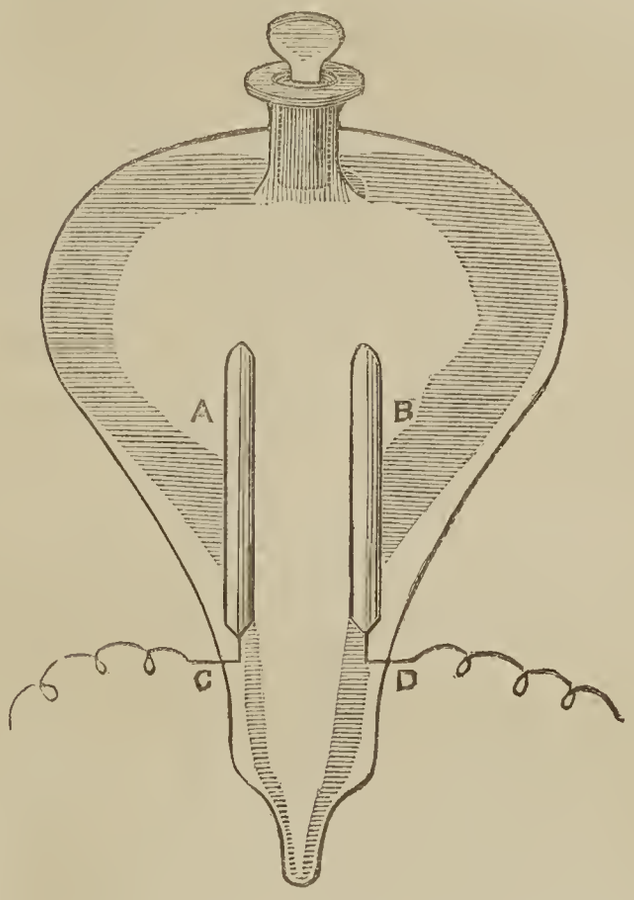
BLEACHING EFFECTS OBSERVED DURING THE ELECTROLYSIS OF ACIDIFIED WATER.

By H. N. WARREN, Research Analyst.

While recently demonstrating upon the electrolysis of water, I caused the acidulated water contained in the voltameter which was employed for that purpose to be coloured blue by the addition of a small quantity of sulphate of indigo, so that the passage into, and, at the same time, the collection of the gases in their respective tubes, might be the more readily observed.

On decomposition of the water being accomplished by the aid of four Bunsen cells, it was observed, after the lapse of a few minutes, to have assumed an entirely greenish tint, which almost directly afterwards completely disappeared, leaving the water perfectly colourless.

After the performance of several experiments, with a view of ascertaining the effects on a more efficient scale, the following apparatus was devised:—As shown in the diagram, it consists essentially of an ordinary separating funnel, into the sides of which are secured, by fusing, two thick platinum wires, namely, C and D; these are connected with two graphite pencils, A and B, the surface of each being prepared by introducing the same into a concentrated solution of platinum nitrate, and afterwards heating to redness, out of contact with air. On connecting the extremities of the platinum wires with a battery consisting of four Bunsen cells, and having, previous to this, introduced into the globe about half a litre



of an acidified and concentrated solution of sulphate of indigo, after the lapse of a quarter of an hour the blue colour, which, at the commencement of the action, was of the usual deep tint natural to indigo, had become transformed into a perfect green, which, as in the former experiments, speedily became colourless. Turmeric, tincture of yellow berries, logwood, cochineal extracts were also as successfully bleached. In a further experiment a piece of indigo dyed cloth was suspended between the carbon poles, and at the termination of two hours was almost destitute of any blue colouration. Several samples of raw yellow cotton were also successfully bleached when exposed to the same action; while nitrogenous products such as wool, and also solutions of the various unrefined sugars, experienced little, if any, change.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

Alcohol in Ethereal Oils.—H. Hager (*Ph. Zeitung*) determines such alcohol approximately by pouring the sample into a narrow test-tube and shaking it well up with pure glycerin. The glycerin rapidly and completely withdraws from the oil any alcohol which is present, and its quantity may be approximately estimated by the increase of the volume of the glycerin. In oils containing acids or similar constituents this method does not give accurate results.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING JULY 31ST, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S.,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, August 10th, 1889.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from July 1st to July 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

One sample, out of the 189 examined, manifested a "very slight turbidity." The remaining 188 samples were found to be clear, bright, and well filtered.

Despite the unfavourable influence of the stormy weather prevailing more or less throughout the month, the condition of the water supply, furnished by each of the seven Companies respectively, was found to be entirely satisfactory. In our report for the previous month of June, we had to record a slight increase in the mean proportion of organic carbon present in the supply, as compared with that present in the supply for the preceding month of May. This slight increase, due, it would seem, to the casual occurrence of a flooded state of the rivers, was not found to be sustained in the supply for the past month of July. Thus, taking the Thames-derived water for comparison, the mean proportion of organic carbon present in 100,000 parts of the water during each of the last three months respectively, was found to be as follows:—

Parts of Organic Carbon in 100,000 *Parts of Water.*

May	0·144
June	0·157
July	0·137

The mean proportion of organic carbon present in the July supply constitutes, accordingly, the lowest monthly mean yet met with during the year; while the maximum proportion met with in any single July sample, or 0·153 part in 100,000 parts of the water, falls a little short of the mean proportion for the preceding month of June—this last proportion, moreover, constituting also the mean proportion for the first six months of the year. The above detailed result of the determination of organic carbon is fully corroborated by the results of the determination of the amounts of oxygen required for the oxidation of the organic matter present in the water, and of the determination of the degree of freedom of the water from colour-tint.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

THE COLOURED REACTION OF CARBON COMPOUNDS.*

By EMIL NICKEL.

THE author points out that the colour-phenomena adduced as the reactions of single bodies are for the most part not confined to the substances in which they were first observed, but such colour-reactions are almost always common to a whole group of bodies if brought in contact with the reagent in question. For the identification of such substances it is therefore necessary to submit them to the action of a number of reagents.

Every kind of coloured reaction seems to point to the presence of a definite group of atoms, and by the combination of several such reactions it is possible not merely to recognise such a body with certainty, but by systematically following out this point of view we may obtain a more or less complete insight into the constitution of the compound in question.

1. *Colour Reactions under the Influence of Nitrous Acid, Exclusive of the Formation of Azo-colours.*

a. Reactions with Millon's Reagent.—For the preparation of the reagent the author finds it most convenient to dissolve 1 c.c. of mercury in 9 c.c. nitric acid of sp. gr. 1·52 and to dilute with an equal volume of water. The effective constituents of the reagent are the mercuric and mercurous nitrates and free nitrous acid. The solution becomes useless on prolonged keeping, but it can be restored by the addition of potassium nitrite. As a rule, 1 or 2 drops of Millon's reagent are to be applied to 1 to 2 c.c. of the solution in question; the colouration comes up best at 60°, 70°, or 100°; in some instances, *e.g.*, thymol, the colour first produced is destroyed by boiling.

As to the substances which yield a colour with Millon's reagent, the author finds that it is always aromatic compounds in which one hydroxyl-group (OH) or the derived methoxyl-group ($O-CH_3$) is fixed on a benzol or naphthaline nucleus.

The reaction occurs also when along with the hydroxyl-group an aldehyd or carboxyl-group or a lateral chain is joined to the benzol nucleus, or even when hydroxyl or amido-groups occur in the lateral chain. But if a nitro-group or a second hydroxyl-group is attached to the benzol nucleus no red colour is produced by Millon's reagent. Thus, resorcine gives a yellow colour, pyrogallol a brown, and hydroquinone an orange. On the other hand, tannin, which contains several hydroxyls bound to the benzol nucleus, gives, with Millon's reagent, a red colour, which soon disappears and is not permanent in heat.

Whilst, therefore, it is not to be expected that compounds which contain simultaneously a hydroxyl-group and a methoxyl-group on the benzol nucleus will give no reaction, there results with guiacol (certainly not chemically pure) a red colour, and with eugenol and vanilline a very decided violet.

Hofmann's Reagent consists of a solution of mercuric nitrate with a trace of free nitrous acid, whilst

c. Plugge's Reagent consists of a solution of mercurous nitrate with a little free nitric acid.

The manner of application and the sphere of action are in both cases analogous to those of Millon's reagent, but in many cases there appear small differences which point to a different behaviour of the two stages of oxidation of the mercury.

d. Liebermann's Colour Reactions.—If 100 parts of sulphuric acid and 5 parts of potassium nitrite are let act upon phenols we obtain, as Liebermann has shown, colourations of different kinds. If the question is not the application of this reaction to the production of colouring-

* An Inaugural Dissertation presented to the Philosophical Faculty of the University of Jena.

matters, but to recognise one or other substance, such substances must be allowed to react in dilute solutions, whilst Liebermann prefers the use of the phenols undissolved, or at least in a concentrated solution.

The author finds that the monophenols are distinguished by the production of intense colours, whilst, among the polyvalent phenols, only orcine yielded a strong red colouration, and the remaining for the most part gave merely a faint yellowness.

Liebermann's reaction resolves itself into two phases. The phenols unite with nitrous acid to nitrosophenols, and the latter, under the condensing influence of the sulphuric acid, form the colouring-matter with the unchanged part of the phenol.

The reaction can therefore be effected by letting phenols, nitrosophenols, and sulphuric acid act upon each other. In this form the reaction is applicable to the nitrosophenols.

e. New Colour-Reactions with New Reagents.—In connection with Liebermann's reaction the author has endeavoured to use, instead of sulphuric acid, other condensing agents, in case of need, with the aid of heat. In this manner he has been led to use various metallic salts of the mineral acids, along with an alkaline nitrite and free acid, although the latter was in many cases not advantageous. These reagents act primarily upon the phenols or the oxy-aromatic compounds. The author makes two reactions especially prominent, though without regarding them as decisive for the organic compounds concerned.

If a solution of vanilline is boiled with a solution of mercuric chloride containing potassium nitrite, there appears, in a few minutes, a fine violet colour. The sensitiveness depends somewhat upon the composition of the reagent, but it is certainly equal to that of the reaction with a solution of an aniline salt.

If we add to a solution of phlorhizine an excess of solid potassium nitrite, then a little solid zinc sulphate, and boil the solution, there appears a blue or violet colour. Some other glycosides which the author examined (coniferine, salicine, quercitrine) displayed, when similarly treated, no colouration.

2. *Coloured Reactions with Formation of Azo-colours.*

a. Weselsky's Reaction and its Extensions.—Weselsky originally recommended the use of potassium nitrite and aniline nitrate for the detection of phloroglucine. Of course another salt of aniline, *e.g.*, the sulphate, can be used as well. The author obtained very fine coloured reactions with salts of toluidine, xylidine, and naphthylamine.

Instead of producing diazo-compounds by mixing the above-named amidic bodies with a nitrite upon the action of which the production of the colour depends, the diazo-compounds may be used directly.

Among bodies not technically important or not exclusively so, Weselsky has observed that phloroglucine, and also catechine and maclurine, yield, with his reagent, red colours. Procter (CHEMICAL NEWS) has sought to ascertain if all the phloroglucides (*i.e.*, the numerous vegetable principles which, on their decomposition, yield phloroglucine) produce this reaction, but without having come to a definite solution of the question.

In his experiments with the phenols carried out as above the author obtained almost exclusively brown or yellow colours. With resorcine he obtained red colours, which differed slightly according to the diazo-compound employed. With phorhizine and with several aldehyds he obtained red colours.

b. Colour-Reactions with Para-diazo-benzol-sulphuric Acid (Ehrlach's Reaction).—The accounts of these colour-reactions relate almost exclusively to the researches of Ehrlich, Petri, Penzoldt, and Fischer and Penzoldt, already given in the *Zeitschrift für Analytische Chemie.*

3. *Colour-Reactions with Formation of Triphenylmethane Colours and Analogous Compounds.*

a. Colour-Reactions of the Phenols with Aldehyds.—The author has chiefly studied the behaviour of phenol, pyrocatechine, resorcine, hydroquinone, pyrogallol, and phloroglucine with aldehyds and some other compounds, and points out that the solutions requisite for such reactions should not be kept, as they readily suffer decomposition. By the direct action of the phenols upon the aldehyds under suitable conditions we scarcely obtain a colouration. This appears only on the simultaneous presence of an acid. The author mentions, as a theoretical basis of this fact, the circumstance that the triphenylmethane colouring-matters in question are distinguished from such compounds as rosaniline, aurine, and phthalein, thereby, that in the former the fourth hydrogen atom of the methane is present unchanged, whilst in the latter compounds it is eliminated or substituted.

The author's attempts to obtain colour-reactions in very dilute cold solutions led to no satisfactory results.

On adding a sufficient quantity of acid and applying heat in case of need the phenols were found to be very useful reagents for aldehyds, though the colour-reactions were not confined to the latter. The author has obtained very fine reactions with nitrogenous bodies, alloxan and creatinin, on boiling with phenols and acids.

b. The Phenols as Reagents for Lignine.—In connection with the above the author shows that probably all the phenols give well-marked colour-reactions with wood in presence of an acid. Nickel considers phloroglucine as the best reagent for wood. An intense violet-red colouration is produced by lignine in contact with phloroglucine and an acid.

c. The Aldehyds as Reagents for the Phenols.—This is merely an inversion of the reactions given under *a*. For the detection of phloroglucine Nickel recommends wood or wood-stuff paper in presence of hydrochloric acid.

d. Salts of Aniline, Toluidine, &c., as Reagents for Aldehyds.—The above substances, either in alcoholic or or aqueous solution or in the solid state, and in general without the presence of acids, yield coloured reactions with a series of substances. As an example, Nickel mentions the yellow colour (first observed by Singer) produced on the contact of a solution of an aniline salt with solutions of the vanilline salts. The reaction is not specific, since it occurs with salicyl-aldehyd. It does not, however, extend to all the aromatic aldehyds, as cinnamol gives no colouration with aniline sulphate.

He discusses the furfurol reactions with aniline sulphate and with xylidine acetate observed by Stenhouse, Jorissen, Förster, and Schiff, and regards the reaction as probably not limited to furfurol.

Benzophenone, acetophenone, and acetacetic ether give no colour with aniline sulphate, though eugenol, which belongs to the phenols, gives a yellow colour.

Among the glycosides, coniferine alone gives a yellow colour with solution of aniline salt, which is faint in solutions, distinct with the solid, and very intense on the addition of acids.

Salts of aniline and toluidine are reagents for lignine.

The presence of potassium bisulphite, which unites with the aldehyds and analogous compounds, prevents the reactions above-mentioned.

The author notices the reactions mentioned by Lustgarten, and shows that they probably belong to the group of reactions just mentioned.

4. *Colour-Reactions with Ferric Salts and with Chromates.*

Ferric chloride, which gives coloured reactions with a great number of organic bodies is best applied in a dilute watery solution.

Among the organic bodies, which give colours with ferric chloride three groups are mentioned.

1. The oxy-aromatic bodies which have an hydroxyl-group at the nucleus.

2. Aromatic bodies containing an amidic group at the nucleus.

3. The carbon acids.

5. *Colour-Reactions with Chromates.*

Setting out from Sanio's proposal to use potassium dichromate for the microchemical detection of the tannic acids, which produces with them a dark red or brown precipitate, Nickel mentions some special cases of tannin reactions, and describes his experiments on the extension of the sphere of these reactions. Some phenols and aromatic azo-compounds have a remarkable behaviour.

Pyrocatechine, according to its concentration, gives, with the alkaline dichromates, a brown or black colour or a dark precipitate. Hydroquinone behaves in the same manner, whilst resorcine gives no colour.

Pyrogallol gives a brown precipitate, and a hot solution of α-naphthol a brown colour. With guaiacol, orcine, and phloroglucine Nickel obtained no reaction. Among the carbon acids gallic acid gives a decided precipitate, whilst pyrocatechuic acid reacts only in strong solutions and forms no precipitate.

As regards the amines, Nickel mentions the brown colour produced by solution of dichromate with aniline and xylidine.

In conclusion the author mentions the colour-reactions produced by the oxidising agency of the dichromate in presence of an acid, and refers here to the behaviour of the alkaloids.—*Zeitschrift für Analytische Chemie*, vol. xxviii., p. 244.

ON PRECIOUS STONES.*

By GEORGE F. KUNZ.

(Concluded from p. 93).

Watch Jewels.—About 1,200,000 watches with jewelled works are annually manufactured in the United States, requiring about 12,000,000 jewels, 7 to 21 for each watch; of these 5,000,000 are ruby and sapphire and 7,000,000 are garnet jewels, valued at over 300,000 dollars. Most of them are imported, but the Waltham Company does its own cutting, employing in this department about 200 hands under the superintendence of Mr. W. R. Wills. About 15,000 carats of bort, in powdered form, are used annually in slitting and drilling these jewels. Nearly all the ruby, sapphire, and garnet used for jewels are imported, but it is hoped that American materials will soon be used. To be of value for this purpose, the material must be of some decided shade of red or blue, of a hardness greater than quartz, and free from flaws.

During the last decade new stones have come into favour, some neglected ones have regained their popularity, and still others, such as the amethyst and cameos, have been thrown out entirely. The latter, no matter how finely cut, would not find purchasers now at one-fifth of their former value; about ten years ago they were eagerly sought after at from four to twenty times the present prices. Rubies were considered high ten years ago, and a further rise was not looked for, but to-day they are still higher, a $9\frac{5}{16}$ carat stone having been quoted at 33,000 dollars. There is no demand at present for topaz, yet a syndicate of French capitalists has been organised to control the topaz mines of Spain, in the expectation that after twenty years of disfavour this gem will again be popular. Coral has felt the change of fashion, for during the last three years the imports have been less than 1000 dollars per annum, and in the last ten years in all 33,956 dollars, whereas in the ten years preceding 388,570 dollars worth were imported. The popularity of amber, on the other hand, is increasing. The imports of amber beads for the ten years 1868 to 1878, amounted to less than 5000 dollars, whereas, during the last ten years 35,897 dollars worth have been introduced. Amber amounting to only 47,000 dollars was imported from 1868 to 1878, but over 350,000 dollars worth from 1878 to 1888. Brazilian pebbles worth 65,000 dollars have been cut or sold ready for re-grinding since 1878, and less than 3000 dollars in the ten years preceding.

Ten years ago few of our jewellers carried more than the following stones in stock:—Diamond, ruby, sapphire, emerald, garnet, and occasionally a topaz or aquamarine. The gem and mineralogical collections contained a large series of beautiful stones, hard, and of rich colour, but known here as "fancy stones," and by the French as *pierres de fantasie*. Since then considerable interest has centered in these fancy stones, and any leading jeweller is not only expected to be familiar with, but to keep almost all of them in stock. This change may be partly referred to the fact that since the Centennial Exhibition art matters have received more attention among us than before.

The Duke of Connaught gave his bride elect a cat's-eye ring as an engagement token; this was enough to make that stone fashionable and to increase its value greatly. The demand soon extended to Ceylon, where the true chrysoberyl cat's-eye is found, and stimulated the search for them there. In the chrysoberyl cat's-eye the effect is the result of a twinning of the crystal, or of a deposit between its crystalline layers of other minerals in microscopic inclusions. If the stone be cut across these layers *en cabochon*, or carbuncle cut, as it is called, a bright line of light will be noticed on the dome-like top of the stone. In price they range from 20 dollars upwards; exceptional stones have sold at from 1000 to 8000 dollars.

In the search for these chrysoberyl cat's-eyes an endless series of chrysoberyls has been found, of deep golden, light yellow, yellow green, dark green, sage-green, yellowish brown, and other tints. They are superb gems, weighing from 1 to 100 carats each, ranking next to the sapphire in hardness. They gave a great surprise to the gem dealers; for it was found that the darker leaf-green or olive-green stones possessed the wonderful dichroitic property of changing to columbine red by artificial light, the green being entirely subdued and the red predominating. They were, in fact, alexandrites, a gem which had formerly been found only in Siberia, and even there of poor quality; though found in large crystals, a perfect gem of even 1 carat was a great rarity. Here, however, fine gems but rarely under 4 carats were found, and an exceptional one weighed 67 carats. They can be numbered among the most remarkable gems known. Strange to say, among this alexandrite variety a few have been found which combine the characteristics of the cat's-eye and the alexandrite, and were accordingly named the alexandrite cat's-eye.

Moonstones also from this same province of Kandy, Ceylon, were brought to light by this search for cat's-eyes. It would not be an over-estimate to say that 100,000 of these stones have been mounted here in the last four years. They vary in size from one-eighth of an inch to nearly 2 inches long and 1 inch thick, and many of them surpass anything hitherto known of their kind in beauty and size, selling from 50 cents to 100 dollars each, in a few exceptional cases 150 dollars. Those displaying the *chatoyant* white and the opalescent blue colour are especially beautiful.

The demand for the cat's-eye also brought into demand the then rare mineral from the Orange river, South Africa, known as crocidolite, more especially that variety that has been altered to a quartz cat's-eye. In this stone an infiltration of siliceous material coated each fibre with quartz or chalcedony, giving it the hardness of 7. This pleasing stone readily sold for 6 dollars a carat, and at the outset for even more; but owing to the excessive competition of two rival dealers, who sent whole cargoes of it to the London market, the price fell to 1 dollar, or even to 25 cents per pound in large quantity. Even table tops have been made of this material by veneering.

* Abstract from "Mineral Resources of the United States."

Vases, cane heads, paper weights, seals, charms, &c., were made of it, and sold in large quantities. Burning it produced a bronze-like lustre, and by dissolving out the brown oxide of iron colouring an almost white substance was obtained, which was dyed by allowing it to absorb red, green, and brown coloured solutions. These, owing to the delicacy of the fibres, were evenly absorbed. Ten years ago this material was practically unknown, but so extensively has it been sold that to-day it is to be found at every tourist's stand, whether on the Rigi, on Pike's Peak, in Florida, at Los Angeles, or at Nishni Novgorod, showing how thoroughly organised is the system of distribution in the gem market. The green quartz cat's-eye from Hof, Bavaria, has also been brought into use and quite extensively sold, but at present both these varieties are only used in the very cheapest jewellery.

Since it has become generally known that Queen Victoria is partial to the opal, the old and stubborn superstition concerning it, which is said to date from Scott's "Anne of Geierstein," has been slowly yielding, until now the gem has its share of public favour. During the last two years ten times as many opals have been imported as were brought here during the preceding decade, many of these being the fine Hungarian stones. Mexican fire opals are much more common, as those tourists know to their sorrow who buy these stones at exorbitant prices in Mexico, hoping thus to pay the expenses of their trip, until they find on reaching New York that they are worth only about a quarter of what they paid for them.

The opal mines of Mexico are situated on the Hacienda Esperenza, near Queretaro. It is believed that a demand of 50,000 stones per annum could be supplied without raising the price perceptibly.

The opal mines of Dubreck, Hungary, yield the Government a revenue of 6000 dollars annually. The output is so carefully regulated that the market is never glutted.

About ten years ago a new and very interesting variety of opal was brought from the Baricoo river, Queensland, Australia, where it was found in a highly ferruginous jasper-like matrix, sometimes apparently as a nodule and then again in brilliant coloured patches, or in specks affording a sharp contrast with the reddish brown matrix, which admits of a high polish and breaks with a conchoidal fracture. Many of these stones are exceedingly brilliant. They are of the variety known as harlequin opals, their colour being somewhat yellow as compared with the Hungarian stone, although not less brilliant. The rich ultramarine blue opal is quite peculiar to this locality, and the green variety almost transcends the Hungarian, A company capitalised at £200,000 has been formed, and the gems are extensively mined. Many curious little cameo-like objects, such as faces, dog's heads, and the like, are made by cutting the matrix and the opal together.

Green beryls, blue and green sapphires, white and bluish topaz, garnets, and zircons have been found at New England, in New South Wales, and precious opals are obtained from the Abercrombie river.

During the last ten years the taste for collecting jade and other carved hard stone objects has greatly increased, especially among Americans, owing to the stimulus given by the Centennial, Paris, and Amsterdam expositions, and the breaking up by sale of many of the large collections. The value of carved jades outside of China and India cannot be far from 2,000,000 dollars.

In the United states there are, perhaps, twenty buyers, who have purchased fully 500,000 dollars worth of this material, many of the pieces being among the finest known, such as the private seal and other objects from the sacking of the Emperor of China's summer palace. The finest pieces, brought over by Tienpau, included some of the best that ever left China, and were intended for the Amsterdam exhibition; the choicest specimens of the Wells, Guthrie, Michael, and Hamilton Palace collections are now owned in the United States. Experienced agents have been frequently sent to India and China to secure the finest objects as they presented themselves. One collection alone is worth over 100,000 dollars; single objects sometimes selling for over 5000 dollars, and one exceptionally fine specimen being valued at over 10,000 dollars. Explorations in Alaska have brought to light the fact that jade was used by the natives for implements, and it is almost proved that it is found not only as boulders but also *in situ*. The National Museum, the Emmons, Everett, Peabody Museum, Canadian Geological Survey, Dresden, and other collections, including the writer's own, contain several hundred objects, at least, that are made of this Alaskan material. A fact of interest in this connection is that Prof. F. W. Clarke found among the objects collected for the National Museum one which, on analysis, proved to resemble pectolite so closely that he referred it to that species. It has the hardness of jade, a specific gravity of 2·873, and is pale green in colour. The same discovery was made almost simultaneously by foreign observers.

The theory that jadeite or chalchiuitl was highly prized by the aborigines has been greatly strengthened during the last ten years. Prof. J. J. Valentine, in his paper before the American Antiquarian Society, April 27, 1881, on the Humboldt celt or votive adze and the Leyden plate, two remarkable carved jadeites, offered some exceedingly interesting suggestions. The Humboldt celt was presented to Humboldt by Del Rio in 1803, and the Leyden plate was given to that museum by A. S. Von Bramm, who found it near St. Felipe, close to the borders of Guatemala, in Honduras. They are both 9 inches in length and $3\frac{1}{4}$ inches wide; the former $1\frac{3}{5}$ inches ia thickness, and the latter only $\frac{1}{5}$ inch. This similarity of dimensions suggests to me that the two objects were originally part of one and the same celt. Before the same Society, in April, 1886, Professor Putnam exhibited his remarkable series of Nicaragua and Costa Rica jadeites, which were all ornaments made by cutting into halves, thirds, or quarters one large celt perforated by one or two drilled holes, in one instance two of them fitting together. The 16-pound adze exhibited by myself at the American Association for the Advancement of Science meeting of 1887, from which fully two pounds had been cut; the breastplate recently found measuring only one-half inch thickness; and the fact that even Burmese jadeite, when burned or exposed to a high temperature, will assume the greyish green colour of the Mexican, all tend to support Professor Fisher's theory that this jadeite originally came from there. Additional evidence is the striking resemblance between the Maya and ancient Burmese styles of carving, although Dr. Meyer, of Dresden, firmly believes that this material will yet be found *in situ* in Mexico. The imperial jade quarries of Burmah, in the Mogung district, 90 miles from Bhamo, are leased by two companies, who pay a royalty of 30,000 dollars annually. The trade is entirely in the hands of the Chinese. At the Colonial Exhibition in London in 1886 there were exhibited large rounded and waterworn blocks of jade weighing hundreds of pounds called panauni by the Maories. Much of it is of the finest green colour and was worked into charms, knife-handles, &c. Dr. W. Buller exhibited a fine collection of Maori ornaments and clubs, or neeris, heitikas, and other native ornaments made of this stone.

Collections of Gems.—A regrettable dispersion of jewels and precious stones took place in May, 1886, when the famous collection formed by the late Henry Philip Hope, and exhibited at the South Kensington Museum for many years, was sold at auction. The Hope collection included the "Saphir Merveilleux" of Madame de Genlis's "Tales of the Castle;" the King of Kandy's cat's-eye, the largest known, having a diameter of $1\frac{1}{2}$ inches; the Mexican Sun opal, carved with the head of the Mexican Sun God, and known since the sixteenth century; an enormous pearl, the largest known, weighing 3 ounces and measuring 2 inches in length; the aqua-marine sword-hilt, made for Murat, the King of Naples; and also many curious

diamonds, sapphires, emeralds, and several hundred unique and magnificent gems. Such a collection should have been preserved intact as a national possession.

In 1886 it was decided by the French Assembly that the Crown jewels, with the exception of the famous "Regent" diamond, two of the Mazarins, and a few historic pieces reserved for the national museums, should be sold at public auction. These exceptions were made because it was feared that they would fall into the hands of Americans. The sale of this great historic collection took place in May, 1887. The forty-eight parcels were subdivided into one hundred and forty-six lots, and there were sixty-eight buyers; the sales to twelve of them brought over 100,000 francs each. The largest lot, the great corsage, which sold for 811,000 francs, was purchased by a single American firm, the largest buyer at the sale. The purchases of this firm amounted to 2,249,600 francs, or about 34 per cent of the entire sum realised; while as to quality the same firm obtained more than two-thirds of the finest gems, among them were three Mazarins; a pear-shaped rose brilliant weighing $24\frac{27}{32}$ carats, for 128,000 francs; a pear-shaped white brilliant weighing $22\frac{1}{4}$ carats, for 81,000 francs; a white brilliant weighing $28\frac{7}{16}$ carats, for 155,000 francs; and an oval brilliant weighing $18\frac{1}{32}$ carats, for 71,000 francs; or 435,000 francs for the four. All but one of their purchases were secured by private American customers. The great interest attached to this sale was due not only to the fact that many of the gems were of very fine quality, but also to their historic associations; the history of many of them could be traced back several hundred years.

The collection of antique gems, numbering three hundred and thirty-one pieces, formed by the late Rev. C. W. King, of Trinity College, England, the greatest of all writers on engraved gems, was sent to the United States for sale in 1881. This collection represents the summing up of Mr. King's vast knowledge, and none has ever been more thoroughly studied. His numerous writings mark an epoch in the study of this branch of archæology, and only the loss of his sight led him to part with his treasure. The growing interest and taste in archæological matters in the United States induced him to send it there to be sold intact. In October, 1881, through the friendly mediation of Mr. Feuardent, it was purchased and presented to the Metropolitan Museum of Art by Mr. John Taylor Johnson, the president of the museum where it now remains. Near it will be placed the Sommerville collection. Mr. Maxville Sommerville, while spending the past thirty-two years of his life in Europe, Asia, and Africa, has collected cameos, intaglios, seals, and other historical gems, and as a result of his liberal expenditure of time and money he is to-day the owner of one of the most unique and valuable collections of engraved gems in the world. It numbers over one thousand five hundred specimens, including Egyptian, Persian, Babylonian, Etruscan, Greek, Roman, Aztec, and Mexican glyptic, or jewel carving art. All of these are represented by specimens of singular excellence, affording us a panoramic view of the achievements of civilised men in this direction. This remarkable collection, now at his home in Philadelphia, has been loaned to the Metropolitan Museum of Art, New York, where it will soon be placed on exhibition, and the public will be afforded every facility to study the beautiful achievements of the glyptic art.

Of greater antiquity and archæological value, because representing a period before gems were cut in the form of intaglios, is the collection of the Rev. W. Hayes Ward, consisting of 300 Babylonian, Persian, and other cylinders. Two hundred of these he himself collected in Babylon and its vicinity, and sold to the museum at a nominal figure. Since that time he has collected 100 more cylinders, many of them date from 2500 B.C. to 300 B.C., and are cut in lapis lazuli, agate, carnelian, hæmatite, chalcedony, jasper, sard, &c.

The death of Dr. Isaac Lea, of Philadelphia, in his ninety-fifth year, deprived the world of a great investigator in the field of precious stones. During the last twenty years of his exceptionally long and useful life, he devoted almost his entire time to studying the microscopic inclusions in gems and minerals, and the cabinet he left contains thousands of specimens of rubies, sapphires, chrysoberyls, tourmalines, garnets, quartz, &c., all of which he had subjected to the most rigid microscopic scrutiny, noting every interesting fact on the accompanying label. Only a small part of his work on this highly interesting subject has been published by the Philadelphia Academy of Sciences in two papers (in 1869 and 1876), but Dr. Lea made ample provision in his will for the publication of the remainder. His extensive collections of minerals and shells were bequeathed to the National Museum, and the gem collection to his daughter. Two months before his death the writer spent two hours with him examining a series of quartz inclusions, over which he worked with all the enthusiasm and brightness of youth.

One of the many benefits traceable to the New Orleans Exposition was the appropriation given to the National Museum for their exhibit. This was wisely expended by Prof. F. W. Clarke in the purchase of a complete series of precious stones, many of which, although not expensive, are still the finest in the United States, from an educational standpoint. Since the exposition, many fine specimens have been added by purchase and donation, especially the diamonds and pearls presented by the Iman of Muscat to President Buchanan, consisting of 138 diamonds and 150 pearls, all of good quality. The collection numbers about 1000 specimens, and embraces almost every known variety of precious stone, many of them very fine examples.

NOTICES OF BOOKS.

Picture-making by Photography. By H. P. Robinson. Second Edition, Revised. London: Hazell, Watson, and Viney, Limited.

This work is a difficult subject to handle in a scientific journal. The author says, doubtless with truth, that "art begins where chemistry and optics leave off." He says to his readers "buy your materials of those whose business it is to supply them, and confine your attention to the study of how to use them."

Against instantaneous photography the author raises an interesting objection, which is substantially that it shows us objects so as the eye never reveals them to us. Consequently they have an unnatural appearance. As he puts it, "the eye of the camera is the eye of man." A photograph of a moving object taken in *less* than that fraction of a second during which impressions remain on the retina is not true to nature as we see it. Still Mr. Robinson fully admits that instantaneous photography is valuable if not abused.

Report of the Fourth Indian National Congress held at Allahabad on the 26, 27, 28, and 29 December, 1888. London: Indian Political Agency.

This Report being in its character exclusively political, and having no bearing upon the interests of physical science, cannot come under the notice of the Chemical News.

Detection of Carbon Monoxide in the Air.—C. de la Harpe and F. Reverdin (*Chemiker Zeitung*) filter the air through slag-wool or cotton and pass it over pure dry iodic acid at 150° and then into a solution of starch-paste in distilled water. The monoxide is thus oxidised to dioxide, and the iodine liberated produces the usual blue colour with starch-paste.

CORRESPONDENCE.

THE INSTITUTE OF CHEMISTRY.

To the Editor of the Chemical News.

SIR,—In a recent criminal trial several chemical experts gave evidence as to processes for detecting arsenic and as to other chemical matters. From the detailed newspaper reports it does not appear that any one of these experts was asked by Counsel whether he was a Fellow or an Associate of the Institute of Chemistry.

The time is come when the Members of the Institute, especially the younger portion of them, expect to find their Association publicly recognised as a licensing body.

Would it, therefore, be too much to ask the Officials of the Institute if they are prepared to enquire whether in any recent trials chemical experts have *not* been requested to state their licensing qualifications before being allowed to give evidence; and, in the event of their not having been so requested, to publicly declare the illegality or inadvisability of the omission?—I am, &c.,

A.I.C.

August 19, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 3.

New Element found along with Cobalt and Nickel.—G. Krüss and F. W. Schmidt.—The substance of this memoir has been already inserted.

Determination of Potassium.—Woussen.—The author does not weigh the potassium-platinum chloride as such, but reduces it by means of sodium formiate and determines the platinum separated.

The Electrolytic Separation of Iron.—Edgar F. Smith.—From the *American Chemical Journal.*

Separation of Cadmium from Zinc and Separation of Zinc, Nickel, Iron, and Manganese.—Ad. Carnot.—From the *Comptes Rendus.*

A Characteristic Reaction of Bismuth.—E. Léger (*Bulletin de la Soc. Chimique de Paris*).

Volumetric Determination of Stannous Compounds.—Adolf Jolles (*Chemiker Zeituug*).—Already inserted.

Determination of Fluorine in Compounds Decomposable by Sulphuric Acid.—H. Lasne.—From the *Bulletin de la Soc. Chimique de Paris*).

Method for Determining the Actual Nitrous Acid in Nitrites.—A. Vivier.—From the *Comptes Rendus.*

Recognition and Distinction of Gallic Acid and Tannin.—L. G. Rawson.—From the CHEMICAL NEWS.

Detection of Saccharine.—E. Börnstein and S. C. Hooker.—A controversy as to the trustworthiness of the method proposed by the former chemist.

Detection of Saccharine.—D. Lindo.—From the CHEMICAL NEWS.

Detection of Antipyrine and Antifebrine (Acetanilide).—D. Lindo.—From the CHEMICAL NEWS.

A New and Very Sensitive Reaction of Morphine.—Lister Armitage.—From the *Pharmaceutical Journal.*

Detection of Rhinanthine.—Dr. T. L. Phipson.—From the CHEMICAL NEWS.

On Kjeldahl's Process for the Determination of Nitrogen.—L. L'Hôte.—From the *Comptes Reudus.*

Determination of Alcohol.—B. Rœse (*Zeitschrift fur Angewandte Chemie*).—The author oxidises with permanganate in presence of sulphuric acid, adding the former reagent at once in excess.

Determination of Glycerin.—A number of methods taken from the *Comptes Rendus*, the *Chemiker Zeitung*, the *Journal of the Society of Chemical Industry*, and other journals.

Examination of Water for Dissolved Gases.—L. W. Winkler (*Berichte*).—The author oxidises an excess of manganous oxide to manganic oxide in presence of alkali by means of the oxygen dissolved in a known weight of water. The quantity of manganic oxide is next determined iodometrically.

Determination of Free and Semi-combined Carbonic Acid in Drinking or Industrial Waters.—Leo Vignon.—From the *Comptes Reudus.*

Detection of "Measles" in Sausages.—Schmidt Mülheim (*Deutsche Med. Zeitung*).—The author digests the sample with an excess of artificial gastric juice.

Examination of Butter.—G. Ambühl (*Chemiker Zeitung*) proposes, for determining the specific gravity of butter-fat at 100°, an apparatus closely resembling that of Soxhlet. For detecting artificial colouring-matters in butter, E. M. Martin proposes a method in the *Analyst.*

Examination of Vermicelli for Foreign Colours.—L. Cavedoni.—Already inserted.

Analysis of Crude Materials containing Tartaric Acid.—Goldenberg, Geromont, and Cie.—The authors reply to the critique of Von Lorenz, and, admitting his objections in case of chemically pure materials, they maintain that in case of lees and crude argols the original method of Goldenberg gives more accurate results than the modified method of Von Lorenz (*Chemiker Zeitung*).

Solubility of Paraffin with reference to its Determination.—Br. Pawlewski and Jak. Filemonowicz.—1 part by weight of paraffin requires for its solution 3856·2 parts of glacial acetic acid. One volume of commercial petroleum dissolves in 8 to 16 vols. of glacial acetic acid, 1 vol. of green oils in 30 to 60, and 1 of petroleum residues in 20 to 50 volumes. Vaseline, ceresine, and ozokerite, like paraffin, are almost insoluble (*Berichte*).

Determination of Neutral Fats.—Max Gröger (*Zeit. Angew. Chemie*).—To obtain accurate results a decided excess of caustic potash must be used for saponification. To 5 grms. fat must be taken such an excess of alkali that not less than 5 c.c. of semi-normal acid are needed for titrating back.

The Detection of Sugar in the Commercial Extract of Logwood.—Otto Schweissinger.—Already inserted.

Determination of Alcohol in Chloroform.—H. Hager.—The author shakes up the sample with glycerin which has been diluted with one-fourth to one-third of its volume of water.

Detection of Antefebrine in Phenacetine.—J. Schröder (*Nederl. Tija. voar Pharm.*).—The author boils 0·5 grm. in 5 to 8 c.c. water, cools, and filters. The filtrate is boiled with dilute nitric acid to which a little potassium nitrite has been added; a few drops of nitric acid containing nitrous acid are added, and the liquid is boiled again. Pure phenacetine undergoes no change, but if 2 per cent of antifebrine are present there is distinct reddening.

Examination of Natural Oil of Bitter Almonds containing Hydrocyanic Acid.—Kremel (*Pharm. Post*).—The author heats with an excess of potassa in alcohol and titrates back with hydrochloric acid. Yellow crystalline benzoin separates out, and is collected, dried, and weighed. It should amount to 40 to 50 per cent of

the sample operated upon. Laurel oil containing hydrocyanic acid and nitrobenzol yield no benzoin.

Adulteration of Balsam of Tolu.—R. A. Cripps.—From the *Pharm. Journal.*

New Process for Determining Urea in Urine.—E. Pflüger and L. Bleibtreu.—This method will be given in detail as soon as possible.

Detection of Free Hydrochloric Acid in Gastric Juice with Methyl-violet.—According to F. Penzoldt and G. Kost (*Medicin Centralblatt*) this method succeeds often only if the gastric juice has been previously precipitated with a 10 per cent solution of tannin.

Detection of Sugar in Urine.—C. Schwarz (*Pharm. Zeitung*).—The author uses the phenylhydrazin test.

Determination of Globuline in Albuminiferous Urine.—D. Kamenski (*Diss. Petersburg* and *Chem. Centralblatt*).—The author modifies Hammarsten's process by saturating the undiluted urine with magnesium sulphate.

Benzoyl Chloride as a Reagent for Cystine, Carbohydrates, and Diamines in Urine.—E. Baumann (*Zeit. Physiol. Chemie*).—Not adapted for useful abridgment.

Determination of Albumenoids with especial reference to Milk.—J. Sebelien (*Zeit. Physiol. Chemie*).—The author precipitates the albumenoids by Ritthausen's process and determines the nitrogen in the precipitate according to Kjeldahl.

Separation of Cocaine from Animal Remains.—U. Mussi (*Orosi*).—The comminuted substance is mixed with 2 parts of alcohol at 90 per cent, acidulated distinctly with hydrochloric acid, digested for a long time at 60° in a reflux condenser, repeating this process with fresh alcohol, evaporating the filtrates almost to dryness at 50° to 60°, taking up the residue with water, shaking out the solution two to three times with ether, precipitating the residual aqueous concentrated liquid with baryta, and extracting repeatedly with ether. The ethereal solution is evaporated in a vacuum and the residue tested for cocaine.

Studies on the Chemico-legal Demonstration of Blood.—A. Klein (An Inaugural Dissertation).—A bulky memoir which does not admit of useful abstraction.

New Reaction for Carbon Monoxide in Blood.—Kuniyosi Katayama (*Chem. Centralblatt*).—Blood containing carbonic oxide after the addition of orange-coloured ammonium sulphide and acetic acid at 30 per cent, takes a fine light red colour, whilst normal blood appears greenish grey or reddish greenish grey.

The Atomic Weight of Copper.—T. W. Richards (*American Academy of Arts and Sciences* and *American Chemical Journal*).—The author's first series of experiments lead to the mean value 63·628 (Ag = 108) or 63·437 (Ag = 107·675). The mean of the two last series shows a value of 63·450 (Ag = 107·65).

Journal de Pharmacie et de Chimie.
Vol. xix., No. 10.

Detection of Nitrates in Potable Waters.—S. C. Hooker.—To 2 c.c. of the water the author adds 4 c.c. of pure strong sulphuric acid, and when the mixture is cold a small quantity of carbazol in sulphuric acid. A green colouration indicates the presence of nitric acid.

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NOTICE.

The STUDENTS' NUMBER of the CHEMICAL NEWS *will be published on Friday, September 20th. Gentlemen holding official positions in the Universities, Medical Schools, &c., of the United Kingdom, where Chemistry and Physical Science form a part of the education, who have not yet forwarded the necessary information to our Office for publication in that Number, will confer a favour by sending it with the least possible delay.*

Advertisements for this Number should reach the Office not later than Wednesday, the 18th prox.

THE CHEMICAL NEWS.

Vol. LX. No. 1554.

ON THE CAVENDISH EXPERIMENT.*

By C. V. BOYS, A.R.S.M., F.R.S.,
Assistant Professor of Physics at the Normal School of Science, South Kensington.

(Concluded from p. 100).

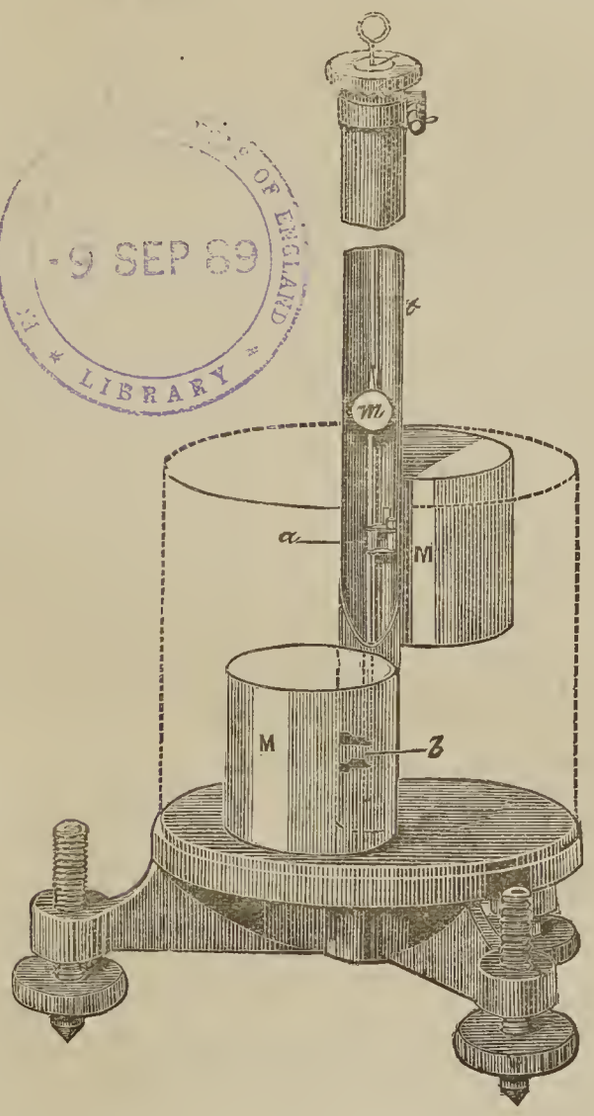
Having found that with apparatus no bigger than an ordinary galvanometer it should be possible to make an instrument far more sensitive than the large apparatus in use heretofore, it is necessary to show that in practice such a piece of apparatus will practically work, and that it is not liable to be disturbed by the causes which in large apparatus have been found to give so much trouble.

I have made two instruments, of which I shall only describe the second, as that is better than the first both in design and in its behaviour.

The construction of this is made clear by the figure. To a brass base provided with levelling screws is fixed the vertical brass tube, *t*, which forms the chamber in which the small masses *a b* are suspended by a quartz fibre from the pin at the upper end. These little masses are cylinders of pure lead 11·3 m.m. long, and 3 m.m. in diameter, and the vertical distance between their centres is 50·8 m.m. They are held by light brass arms to a very light taper tube of glass, so that their axes are 6·5 m.m. from the axis of motion. The mirror, *m*, which is 12·7 m.m. in diameter, plane and of unusual accuracy, is fastened to the upper end of the glass tube by the smallest quantity of shellac varnish. Both the mirror and the plate-glass window which covers an opening in the tube were examined and afterwards fixed with the refracting edge of each horizontal, so that the slight but very evident want of parallelism between their faces should not interfere with the definition of the divisions of the scale. The large masses, M M, are two cylinders of lead 50·8 m.m. in diameter, and of the same length. They are fastened by screws to the inside of a brass tube, the outline of which is dotted in the figure, which rests on the turned shoulder of the base so that it may be twisted without shake through any angle. Stops (not shown in the figure) are screwed to the base, so that the actual angle turned through shall be that which produces the maximum deflection. A brass lid, made in two halves, covers in the outer tube and serves to maintain a very perfect uniformity of temperature in the inner tube. Neither the masses, M M, nor the lid touch the inner tube. The period of oscillation is eighty seconds.

With this apparatus placed in an ordinary room with draughts of air of different temperatures, and with a lamp and scale such as are used with a galvanometer, the effect of the attraction can easily be shown to a few, or, with a lime-light, to an audience. To obtain this result with apparatus of the ordinary construction and usual size is next to impossible, on account chiefly of the great disturbing effect of air currents set up by difference of temperature in the case. The extreme portability of the new instrument is a further advantage, as is evident when the enormous weight and size of the attracting masses in the ordinary apparatus are considered.

However, this result is only one of the objects of the inquiry which I have now the honour to submit to the Royal Society. The other object which I had in view was to find whether the small apparatus, besides being more sensitive than that hitherto employed, would also be more free from disturbances and so give more consistent results. With this object I have placed the apparatus in a long narrow vault under the private road between the Museum and the Science Schools. This is not a good place for experiments of this kind, for when a cab passes overhead the trembling is so great that loose things visibly move; however, it is the only place at my disposal that is in any degree suitable. A large drain pipe filled with gravel and cement and covered by a slab of stone forms a fairly good table. The scale is made by etching millimetre divisions on a strip of clear plate-glass 80 c.m. long. This is secured at the other end of the vault at a distance of 1053·8 c.m. from the mirror of the instrument. A telescope 132 c.m. long, and with an object-glass 5·08 c.m. in diameter, rests on V's clamped to the wall, with its object-glass 360 c.m. from the mirror. Thus any disturbance that the observer might produce if



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nearer is avoided, and at the same time the field of view comprises 100 divisions. While the observer is sitting at the telescope he can by pulling a string move an albo-carbon light mounted on a carriage so as to illuminate any part of the scale that may happen to be in the field of the telescope. The white and steady flame forms a brilliant background on which the divisions appear in black. The accuracy of the mirror is such that the m.m. divisions are clearly defined, and the position of the cross-wire (a quartz fibre) can be read accurately to one-tenth of a division. This corresponds to a movement of the mirror of almost exactly one second of arc.

The mode of observation is as follows:—When all is quiet with the large masses in one extreme position, the position of rest is observed and a mark placed on the scale. The masses are moved to one side for a time and then replaced, which sets up an oscillation. The reading of every elongation and the time of every transit of the

* Extracts from a Paper read before the Royal Society, June 20, 1889.

Elongation.	Amplitude.	Decrement.	True position of rest.	Time of transit of 36·09. h. m. s.	Correction for transit of true position of rest.	True half period.
15·05						
	38·15		36·18	9 8 25·0	+0·08	
53·20		0·805				80·2
	30·72		36·20	9 45·5	−0·18	
22·48		0·808				80·2
	24·80		36·21	11 5·3	+0·24	
47·28		0·807				80·0
	20·00		36·20	12 25·8	−0·28	
27·28		0·807				79 9
	16·12		36·22	13 45·0	+0·41	
43·40		0·805				80·1
	12·98		36·21	15 6·0	−0·47	
30·42		0·806				80·1
	10·46		36·22	16 25·0	+0·63	
40·88		0·802				79·5
	8·38		36·24	17 46·0	−0·91	
32·50		0·808				80·5
	6·77		36·24	19 4·5	+1·13	
39·27		0·808				79 8
	5·47		36·26	20 27·0	−1·58	
33·80		0·814				80·5
	4·45		36·26	21 44·0	+1·94	
38·25						
		0·8066				80·08

mark are observed until the amplitude is reduced to three or four c.m. The masses are then moved to the other extreme position and the elongations and transits observed again, and this is repeated as often as necessary.

On the evening of Saturday, May 18th, six sets of readings were taken, but during the observations there was an almost continuous tramp of art students above, producing a perceptible tremor, besides which two vehicles passed, and coals were twice shovelled in the coal-cellar, which is separated from the vault in which the observations were made by only a four and a half inch brick wall. The result of all this was a nearly perpetual tremor, which produced a rapid oscillation of the scale on the cross-wire, extending over a little more than 1 m.m. This increased the difficulty of taking the readings, but to what extent it introduced error I shall not be able to tell until I can make observations in a proper place.

In spite of these disturbances, the agreement between the deflections deduced from the several sets of observations and between the periods is far greater than I had hoped to obtain, even under the most favourable conditions. In order to show how well the instrument behaved, I have copied from my note-book the whole series of figures of one set, which sufficiently explain themselves. (See Table above).

It will be noticed that the true position of rest is slightly rising in value, and this rise was found to continue at the rate of 0·36 c.m. an hour during the whole course of the experiment, and to be the same when the large masses were in the positive or negative position. The motion was perfectly uniform, and in no way interfered with the accuracy of the experiments. It was due, I believe, to the shellac fastening of the fibre, for I find that immediately after a fibre has been attached this movement is very noticeable, but after a few days it almost entirely ceases; it is, moreover, chiefly evident when the fibre is loaded very heavily. At the time that the experiment was made the instrument had only been set up a few hours.

The mean decrement of three positive sets was 0·8011, and of three negative sets 0·8035. The observed mean period of three positive sets was 79·98, and of three negative sets, 80·03 seconds, from both of which 0·20 must be deducted as the time correction for damping.

The deflections obtained from the six sets of observations, taken in groups of three, so as to take into account the effect of the slow change of the position of rest, were as follows:—

From sets 1, 2, and 3	17·66 ± 0·01
„ 2, 3, and 4	17·65 ± 0·02
„ 3, 4, and 5	17·65 ± 0·02
„ 4, 5, and 6	17·65 ± 0·02

An examination of these figures shows that the deflection is known with an accuracy of about one part in two thousand, while the period is known to the four thousandth part of the whole. As a matter of fact the discrepancies are not more than may be due to an uncertainty in some of the observations of half a millimetre or less, a quantity which, under the circumstances, is hardly to be avoided.

The result of these experiments is complete and satisfactory. As a lecture experiment the attraction between small masses can be easily and certainly shown, even though the resolved force causing motion is, as in the present instance, no more than the 1-200,000th of a dyne, (less than 1-10,000,000 of the weight of a grain), and this is possible with the comparatively short half period of eighty seconds. Had it been necessary to make use of such half periods as three to fifteen minutes which have been employed hitherto, then, even though a considerable deflection were produced, this could hardly be considered a lecture experiment.

The very remarkable agreement between successive deflections and periods shows that an absolute measure made with apparatus designed for the purpose, but on the lines laid down above, is likely to lead to results of far greater accuracy than any that have been obtained. For instance, in the original experiment of Cavendish there seems to have been an irregularity in the position of rest of one-tenth of the deflection obtained, while the period showed discrepancies of five to fifteen seconds in seven minutes. The experiments of Baily made in the most elaborate manner were more consistent, but Cornu was the first to obtain from the Cavendish apparatus results having a precision in any way comparable to that of other physical measurements. The three papers published by him in the *Comptes Rendus* of 1878, referred to above, contain a very complete solution of some of the problems to which the investigation has given rise. The agreement between the successive values, decrement, and period is much the same that I have obtained, nevertheless the means of the summer and of the winter observations differ by about 1 per cent.

I have not referred to the various methods of determining the constant of gravitation in which a balance, whether with the usual horizontal beam or with a vertical beam on the metronome principle, is employed. They are essentially the same as the Cavendish method, except that there is introduced the friction of the knife-edges and the unknown disturbances due to particles of dust at these points, and to buoyancy, without, in my opinion, any compensating advantage. However, it would appear that if the experiment is to be made with a balance the considerations which I have advanced in this paper would point to the advantage of making the apparatus small, so that attracting masses of greater proportionate size may be employed, and the disturbance due to convection reduced.

It is my intention, if I can obtain a proper place in which to make the observations, to prepare an apparatus specially suitable for absolute determinations. The scale will have to be increased, so that the dimensions may be

determined to a ten-thousandth part at least. Both pairs of masses should, I think, be suspended by fibres or by wires, so that the distance of their centres from the axis may be accurately measured, and so that in the case of the little masses the moment of inertia of the beam, mirror, &c., may be found by alternately measuring the period with and without the masses attached. The unbalanced attractions between the beam, &c., and the large masses, and between the little masses and anything unsymmetrical, about the support of the large masses, will probably be more accurately determined experimentally by observing the deflections when the large and the small masses are in turn removed, than by calculation.

If anything is to be gained by swinging the small masses in a good Sprengel vacuum, the difficulty will not be so great with apparatus made on the scale I have in view, *i.e.*, with a beam about 5 c.m. long, as it would with large apparatus. With a view to reduce the considerable decrement, I did try to maintain such a vacuum in the first instrument, in which a beam 1·2 c.m. long was suspended by a fibre so fine as to give a complete period of five minutes, but though the pump would click violently for a day perhaps, leakage always took place before long, and so no satisfactory results were obtained.

With an apparatus such as I have described, but arranged to have a complete period of six minutes, it will be possible to read the scale with an accuracy of one ten-thousandth of the deflection, and to determine the time of vibration with an accuracy about twice as great.

NOTE ON A NEW CRYSTALLINE HYDRATE OF THALLIC OXIDE.

By DOUGLAS CARNEGIE, M.A.

When determining sulphur in galena by the potash and nitre-fusion method I have frequently found that considerable quantities of "red lead" are formed if the fusion be long continued, or if the vessel in which the fusion takes place be left uncovered. The excess of oxygen in the "red lead" above that required by the formula PbO was variable, showing increase with time of fusion. This observation led me to attempt the formation of PbO_2 from litharge by long-continued fusion of the latter with potash and nitre. Not only was this attempt successful, but I soon found that nitre is not essential for this oxidation; the oxygen of the air will do equally well.

Litharge added slowly to fusing potash dissolves in large quantity, and if the resulting potassium plumbite be strongly heated for some time, freely exposed to the air the while, it is completely oxidised to potassium plumbate. On extracting the cooled fuse with water, a colourless, strongly oxidising solution is obtained which has properties greatly resembling those of an alkaline hypochlorite solution. If such a solution is treated with excess of dilute HClAq, chlorine is evolved; if a small quantity of litharge is suspended in it and the mixture then warmed, the litharge is changed to peroxide of lead, while potassium plumbite remains in solution; if treated with $MnSO_4Aq$, a dark brown precipitate of manganese peroxide is formed.

If the solution is *carefully neutralised* with dilute H_2SO_4Aq, a brown precipitate of PbO_2H_2O is thrown down. This is probably the same hydrate that Becquerel obtained at the positive electrode on electrolysing strongly alkaline solutions of lead salts (*Ann. Chem. Phys.* [3], viii., p. 405). If the H_2SO_4Aq be added rapidly and in excess, chlorine is evolved and $PbSO_4$ is precipitated. The appearance of chlorine in this case I would attribute to the presence, in commercial potash, of considerable quantities of chlorides, which, as is well known, by interacting with H_2SO_4 in the presence of a peroxide, give rise to free chlorine.

Now the "ornithorhynchus of the elements"—thallium—shows many analogies with lead, and it occurred to me that still other analogies might be added to the list if the behaviour of the lower oxidised compounds of thallium, when subjected to the action of molten potash, were investigated. The more sanguine was I on account of recent experiments referred to in the Chemical Society's Abstracts for 1888; these experiments, though failing in the actual isolation of a peroxide of thallium (TlO_2), nevertheless, according to the author, clearly pointed to the existence of such an oxide. But as a matter of fact no analogy exists between thallium and lead in this connection.

In my experiments I made hydrated thallic sesquioxide (prepared by Messrs. Harrington, of Cork) my starting-point. If this be dropped slowly and with constant stirring into molten potash,* a small quantity dissolves, and a clear yellow fuse, which probably contains a potassic thallite, results. This salt is, however, very unstable, for if the molten potash be allowed to cool as soon as it has dissolved the maximum quantity of thallic oxide, and the fuse then extracted with water, decomposition ensues and a red-brown precipitate of hydrated thallic sesquioxide separates. This behaviour is pretty much what one would anticipate on recalling the position of thallium in Group III. of Mendeleeff's periodic classification, and the well-founded generalisation in connection therewith, viz., that as the atomic weights of the elements of a group increase, the acidic nature of the corresponding oxides decreases.

If, however, the heating of the clear yellow fuse obtained as above be long continued, beautiful crystalline plates separate. After cooling, the fuse is extracted with water and the crystals washed repeatedly by decantation, first with boiling water till free from adhering potash, and finally with alcohol. The crystals, dried at 100°, give off a mere trace of chlorine when distilled with HClAq (*vide* next paragraph), and contains 80·38 per cent of thallium. The value given is a mean of several concordant results obtained—

(1) By previous reduction to thallous salt, followed by titration with permanganate in presence of a sufficiency of dilute HClAq;

(2) By previous reduction to thallous salt, followed by precipitation of thallous iodide, which was then collected on a tared filter;

(3) By a new volumetric iodometric method for the direct determination of thallium in thallic salts, the details of which I hope to communicate as soon as I shall have completed a more thorough test of its accuracy and general applicability.

The substance is evidently $Tl(OH)_3$ or $Tl_2O_3.3H_2O$, which requires 80 per cent thallium. It it extremely light and forms a brown glistening mass composed of microscopic and exceedingly regular hexagonal plates transmitting yellow light. It is easily soluble in dilute HClAq and H_2SO_4Aq, but generally slight reduction to thallous salt occurs during solution (see *ante*). It is an exceedingly stable hydrate, and is unaffected by exposure to a temperature of 340° C. In this last respect the new hydrate (hydroxide?) contrasts strongly with the only other hydrate of thallium which has up to the present been recognised, viz., $Tl_2O_3.H_2O$; for, according to Carnelley (*Chem. Soc. Journ. Trans.*, 1888), $Tl_2O_3.H_2O$ begins to lose water at 100°, and is completely dehydrated at 230°.

It is interesting to note in this connection that aluminium—the first member of the sub-group of Group III. containing thallium—also forms a crystalline hydrate which loses its water only at a red heat. This hydrate has the composition $Al_2O_3.3H_2O$ or $Al(OH)_3$ (Becquerel "Ency. Chim.," iii., p. 190).

Gonville and Caius College,
Cambridge.

* The fusions were always conducted in a nickel dish which had been internally superficially oxidised (blackened) through long-continued contact with molten potash at high temperature. Nickel always superior to silver for fusions in air, acquires, I find, a vast superiority when thus "protected."

NOTE ON A NEW ALKALOID.*

By JOHN TSAWOO-WHITE.

In extracting in a poisoning case some food forwarded by the District Superintendent of Police, Bassein, by Otto-Stas's method for alkaloids, an amorphous substance was obtained, giving a purple colour with sulphuric acid and oxidising agents like potassium chromate and manganese dioxide. This reaction is supposed to be peculiar to strychnine and curarine, but this substance differs in some respects from these alkaloids. It is a slightly yellowish substance, amorphous, almost tasteless, and not bitter. It dissolves in water, alcohol, and in ether. Its solution in water is not alkaline, giving precipitates with iodine in potassium iodide with Meyer's reagent and with phosphomolybdic acid. It gives no reaction with nitric acid, and none with ferric chloride.

When I showed this substance and its strychnine-like reaction to Dr. Romanis, he tried the action of gold and platinum chlorides on it. Gold chloride gives a white precipitate which decomposes on standing, as it becomes dark coloured. It gives a precipitate of acicular crystals with platinum chloride.

It is a pity that so little of the substance could be obtained in a case like this, that no definite conclusion as to the nature of this probably alkaloidal substance can be drawn. The only thing that can be done is to record it so that, might we stumble on it again unawares, it would be no longer again elusive.

In the last report, just published, of the Chemical Examiner to Government, Burma, is given a short account of this substance.

Rangoon, July 30, 1889.

SPECIFIC VOLUME OF CAMPHOR AND OF BORNEOL DETERMINED WITH PROXIMATE ACCURACY.

By MITSURU KUHARA, Ph.D.

The materials employed in the experiments were ordinary commercial camphor and borneol, purified by repeated sublimation. Their melting- and boiling-points† were found to be as follows:—

	Melting-point.	Boiling-point.
Camphor	177·7°	205·3°
Borneol	—	209·7°

In these determinations a number of experiments were repeated, and in each necessary corrections were made.

The determination of the specific gravity of liquid camphor and of liquid borneol was made with the use of a cylindrical specific gravity bottle of a small size, whose capacity had carefully been ascertained by filling it with boiled distilled water. Either the camphor or the borneol was fused in a long cylindrical vessel over the paraffin-bath, and the specific gravity bottle and its stopper, tied separately with platinum wire, were both introduced into this cylindrical vessel and heated together with the melted camphor or borneol. As the boiling point of the liquid camphor and of the liquid borneol is always found a few degrees higher than that of the vapour, the moment the temperature of the liquid reached 205·3° or 209·7° (boiling-points of their vapours), the stopper was instantly closed and the bottle filled with the liquid was taken out, cooled, and weighed. These experiments were conducted under a higher barometric pressure than the normal, all the measurements being made by means of the corrected thermometer. The specific gravity was calculated according to the following formula referring to the water of 4°.

$$\text{Specific gravity} = \frac{W}{V(1+3\beta(T-t)}$$

W = Weight of the liquid camphor or borneol at T.
T = Boiling-point of camphor or borneol.
V = Volume of water at t (or the capacity of the bottle at t).
t = Temperature when the bottle filled with water was weighed.
3β = Coefficient of the cubical expansion of glass = 0·0000254.

I. *Experiments on Camphor*, $C_{10}H_{16}O$.

The following three experiments were performed with a bottle of the capacity of 6·28114 c.c. at 30·5°.

1. Camphor in the bottle weighed 5·1304 grms. at 205·3°.
2. ,, ,, ,, 5·1089 ,, ,,
3. ,, ,, ,, 5·1189 ,, ,,

The fourth experiment was performed with a bottle of the capacity of 2·98632 c.c. at 40·5°.

4. Camphor in the bottle weighed 2·4252 grms. at 205·3°.

Seven more experiments were performed with a bottle of the capacity of 2·74518 c.c. at 40·5°.

5. Camphor in the bottle weighed 2·2400 grms. at 205·3°.
6. ,, ,, ,, 2·2470 ,, ,,
7. ,, ,, ,, 2·2405 ,, ,,
8. ,, ,, ,, 2·2330 ,, ,,
9. ,, ,, ,, 2·2355 ,, ,,
10. ,, ,, ,, 2·2290 ,, ,,
11. ,, ,, ,, 2·2315 ,, ,,

Specific gravity at 205·3° deduced according to the formula given above:—

1.	0·8131
2.	0·8097
3.	0·8113
4.	0·8087
5.	0·8125
6.	0·8147
7.	0·8127
8.	0·8100
9.	0·8109
10.	0·8085
11.	0·8094
Mean	0·8110

$$\text{Specific volume} = \frac{\text{Molec. wt.}}{\text{Spec. grav.}} = \frac{152}{0{\cdot}811} = 187{\cdot}42$$

II. *Experiments on Borneol*, $C_{10}H_{18}O$.

The experiments were performed with a bottle of the capacity of 2·74518 c.c. at 40·5°.

1. Borneol in the bottle weighed 2·2284 grms. at 209·7°.
2. ,, ,, ,, 2·2284 ,, ,,
3. ,, ,, ,, 2·2265 ,, ,,
4. ,, ,, ,, 2·2245 ,, ,,
5. ,, ,, ,, 2·2390 ,, ,,
6. ,, ,, ,, 2·2258 ,, ,,

Specific gravity at 209·7°.

1.	0·8082
2.	0·8082
3.	0·8075
4.	0·8071
5.	0·8120
6.	0·8073
Mean	0·8083

$$\text{Specific volume} = \frac{\text{Molec. wt.}}{\text{Spec. grav.}} = \frac{154}{0{\cdot}8083} = 190{\cdot}5$$

* Contribution from the Laboratory of the Chemical Examiner, Burma.

† In most text-books the melting and boiling-points of camphor are given to be 174° and 204°, respectively, and the boiling-point of borneol to be 212°.

	Found.			Calculated.	
	Kopp.	Ramsay.	Yoshida.	C=14 and 11; H=3·5; O=12·2 and 7·8.	C=11; H=5·5; O=12·2 and 7·8.
Benzene	95·8	95·9	—	86·0	99·0
Phenol	103·6	106·9	—	103·8	106·9
Benzylalcohol	123·7	—	—	121·8	128·8
Benzaldehyd	118·4	—	—	119·2	122·2
Ethyl benzoate	172·4—174·8	—	163·1*	162·0	174·0
Benzoic acid	126·9	—	—	127·0	130·0
Naphthalene	149·2	—	—	150·0	154·0

* This number was observed according to Ramsay's method by Mr. H. Yoshida, Science College, Imperial University of Tokio.

Specific volume of camphor and of borneol calculated with Kopp's values of the atomic volumes of carbon, hydrogen, and oxygen, supposing the former as a ketone and the latter as an alcohol, is found to be as follows:—

Camphor.

C_{10}	10 × 11	= 110
H_{16}	16 × 5·5	= 88
O	1 × 12·2	= 12·2
Specific volume		210·2

Borneol.

C_{10}	10 × 11	= 110
H_{18}	18 × 5·5	= 99
O	1 × 7·8	= 7·8
Specific volume		216·8

Thus it is seen that the calculated values are much greater than those found by experiments. Also the specific volume of benzene and of some of its derivatives calculated with Kopp's values is often found to be much greater than those obtained experimentally. In Watts's "Dictionary of Chemistry," 3rd Supplement, page 2126, the following statements are given:—"Lothar Meyer makes H=3, and Löschmidt C=14 and H=3·5; and by assuming that half the carbon atoms in benzene have the value 11 and the remainder the value 14, and that hydrogen has the constant value 3·5, we obtain a value for this hydrocarbon which is identical with the observed values." Thus:—

	Calculated.		Found.	
			Kopp.	Ramsay.
C_3	3 × 14 = 42	96	95·8	95·9
C_3	3 × 11 = 33			
H_6	6 × 3·5 = 21			

I tried to apply these values of carbon and hydrogen and Kopp's values of oxygen (12·2 and 7·8) to camphor and borneol, supposing each to consist of a closed chain of six carbon atoms, like benzene, and I found that the calculated specific volumes are almost concordant with those observed.

Camphor.

	Calculated.	Found.
C_3 = 3 × 14		
C_7 = 7 × 11		
H_{16} = 16 × 3·5	187·2	187·42
O = 1 × 12·2		

Borneol.

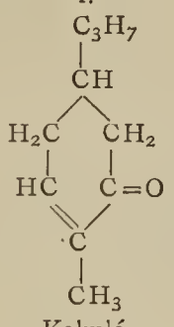
	Calculated.	Found.
C_3 = 3 × 14		
C_7 = 7 × 11		
H_{18} = 18 × 3·5	189·8	190·5
O = 1 × 7·8		

I tried further to compute the specific volumes of some of the benzene derivatives whose experimental numbers are already known, by applying similar methods of calculation to them (see Table above).

It thus appears that the numbers found by the new way of calculation agree better with the observed ones, in some cases, than with those calculated with Kopp's values.

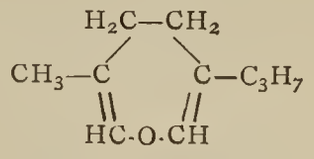
Now the principal formulæ for camphor suggested by different chemists are six in number, namely:—

I.*



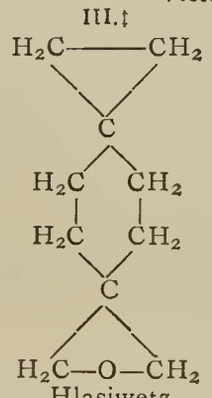
Kekulé.

II.†



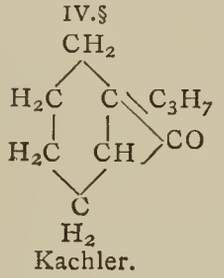
Victor Meyer.

III.‡



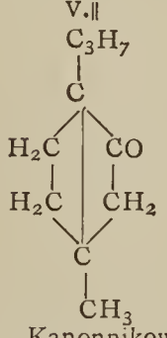
Hlasiwetz.

IV.§



Kachler.

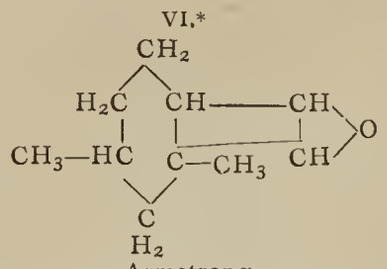
V.‖



Kanonnikow.

* *Ber. d. Deut. Chem. Gesell.*, vi., 929.
† *Ibid.*, iii., 116.
‡ *Ibid.*, iii., 540.
§ *Annalen d. Chem.*, clxv., 185.
‖ *Ber. d. Deut. Chem. Gesell.*, xvi., 3051.

VI.*



Armstrong.

If we suppose the above method of calculation to be true, there may exist in camphor a closed chain of six carbon atoms, and camphor itself may be a ketone, and then the formula I., IV., or V. may represent its constitution, as any one of the remaining formulæ would represent it as an oxide. Kanonnikow,† however, who determined the refraction equivalent of camphor and of its allied compounds by applying Bruhl's method, states that camphor has no double union between carbon atoms. Hence it may be concluded that one of the formulæ IV., and V. represent the constitution of camphor, and borneol is its corresponding alcohol. — *Journal of the Tokyo Chemical Society*, Vol. ix., No. 9.

ON KOBELLITE FROM OURAY, COL., AND THE CHEMICAL COMPOSITION OF THIS SPECIES.‡

By HARRY F. KELLER.

The sulphobismutites and sulphostibnites of the south-western part of Colorado have repeatedly formed the subject of mineralogical and chemical research. Genth, Kœnig, Hillebrand, and others have proved the occurrence there of a number of species already known from other localities, and have also described several new compounds of this class under the names of schirmerite, alaskite, and beegerite.

In the following pages I desire to give the description of a mineral possessing the composition—

$$2(Pb,Ag_2,Cu_2)S,\ (Bi,Sb)_2S_3,$$

and to show further that it is in all probability identical with the kobellite of Setterberg.

The material for this investigation was kindly supplied by my brother, Mr. Hermann A. Keller, of Pueblo, Col. It consisted of several beautiful specimens of an ore that had been taken from the Silver Bell mine, at Ouray, Col., by Mr. Philip Decker.

I have not been able to obtain any further information concerning the occurrence of the mineral, but consider it highly probable that it is closely analogous to that of alaskite described by Kœnig.§ Like this it is found associated with barite and chalcopyrite.

Physical Properties. — Massive. Structure, finely granular, inclining to fibrous; lustre, silky metallic; colour, bluish lead-grey; fracture, uneven; streak, iron-black; apparent hardness, 2·5—3; sp. gr., 6·334.

Chemical Deportment.—Upon heating, the mineral first decrepitates violently and then fuses. In the open tube, it gives off sulphurous acid and a sublimate of antimonious acid. Upon charcoal it yields a yellow incrustation, with a white non-volatile fringe and a metallic globule, which for the greater part is volatilised upon continued blowing.

The residue gives the reactions of iron and copper in the salt of phosphorous bead, and a button of metallic silver on cupellation. A crimson coating is obtained with potassium iodide and sulphur on charcoal.

Hydrochloric acid decomposes the compound with evolution of hydrogen sulphide, especially upon heating; the gangue material and chalcopyrite are left undissolved, while the silver passes into solution, from which it can be precipitated as chloride by diluting with water.

Chlorine, as well as nitric acid, exerts a powerful action upon it.

As the quantitative separation and estimation of the constituents presents some difficulties, I will briefly indicate the course of an analysis which was found to be best adapted to this end. A portion of the mineral was treated with nitric adid. When proper care is taken, the oxidation is completed in an hour's time. The excess of the acid was then removed upon the water-bath and the residue boiled with a solution of pure carbonate of soda. This treatment was continued until all the sulphuric acid, excepting the small quantity in the barite of the gangue, had passed in solution. The undissolved oxides and carbonates of the metals were then filtered off. The filtrate showed a bluish colour, and was found to contain small quantities of copper, antimony, and bismuth. These were precipitated by hydrogen sulphide, after acidifying with hydrochloric acid, and the sulphur then determined in the filtrate as barium sulphate. This was purified, after ignition, by heating with hydrochloric acid, then dissolving it in concentrated sulphuric acid, and re-precipitating it finally with water.

The separation of the metals was effected as follows:— The mixture of the oxides and carbonates, &c., was treated with nitric and tartaric acids, whereby only the gangue material ($BaSO_4$) remained undissolved. After the small quantity of sulphides before mentioned had likewise been taken up in the solution, the silver was precipitated as chloride in the cold; potassium hydrate was then added to the filtrate in excess, and hydrogen sulphide passed into it. The precipitate, consisting of the sulphides of all the metals except antimony, was filtered off, and the antimony determined in the liquid according to Bunsen's method as pentasulphide. The conversion of the pentasulphide into tetroxide served as a check, but gave invariably a slightly lower percentage.

The metallic sulphides were again oxidised with nitric acid, the latter removed by evaporation with sulphuric acid, and the remaining sulphates treated with dilute sulphuric acid (1 : 8) in the cold. In this manner the lead is separated from the other metals, but not completely, as the insoluble sulphate always contains small quantities of bismuth. It is therefore dissolved in warm potash solution, which leaves the oxide of bismuth with some lead, and these can then be separated readily by a renewed treatment with nitric and sulphuric acids.

In the solution containing the sulphates of copper, bismuth, iron, and zinc, the two first mentioned were precipitated as sulphides with hydrogen sulphide, filtered off, converted into the nitrates, and separated from each other with ammonia and ammonium carbonate. Zinc and iron were finally separated and determined by the usual methods.

In order to ascertain which of the metals enter into the composition of the mineral, one portion of the substances (Analysis II.) was dissolved in hydrochloric acid and the residue remaining analysed separately.

Although chlorine acts strongly upon the finely divided powder, I did not succeed in effecting a complete decomposition by its means. All the samples analysed were taken from different pieces of the ore.

	Analyses.					
	I.	II.	III.	IV.	V.	Mean.
S	18·37	—	18·46	18·33	18·39	18·39
Bi	27·97	28·51	28·68	28·46	—	28·40
Sb	7·19	7·25	7·91	7·84	—	7·55
Pb	36·11	36·08	36·25	36·20	—	36·16
Ag	3·22	3·39	3·30	3·32	—	3·31
Cu	2·43	2·26	2·91	2·76	—	2·59
Fe	1·31	1·35	1·69	1·65	—	1·50
Zn	0·50	0·37	0·41	0·31	—	0·39
$BaSO_4$, &c.	0·43	0·65	0·21	0·49	—	0·45
	97·53		99·82	99·36		98·74

* *Ber. d. Deut. Chem. Gesell.*, xi., 1698.
† *Ibid.*, xvi., 3051.
‡ Read at the Meeting of the Chemical Section of the Franklin Institute, May 21, 1889.
§ *Amer. Phil. Soc.*, June. 1881.

In No. II. the portion insoluble in hydrochloric acid was found to contain (after the chloride of silver had been removed by ammonia):—

Fe, 1·09 Cu, 1·12 Zn, 0·24

It seems therefore safe to assume* that the iron and an equivalent quantity of copper are present as chalcopyrite, and the zinc as sphalerite.

Now, deducting these, plus the gangue and the loss, the percentage composition calculated from the mean results is as follows:—

		Atomic ratio.		
S	= 17·76	0·5550		= 2·660
Bi	= 30·61	0·1457	0·2134	= 1·000
Sb	= 8·13	0·0677		
Pb	= 38·95	0·1881		
Ag	= 3·58	0·0166	0·2124	= 0·995
Cu	= 0·97	0·0077		
	100·00			

and the formula is therefore $2(Pb,Ag_2,Cu_2)S$, $(BiSb)_2S_3$. Since the atomic ratio of antimony† to bismuth is 1 : 2 the mineral may be considered as composed of 1 mol. of jamesonite with 2 mols. of cosalite.

The recent text-books of mineralogy do not assign this formula to any mineral, nevertheless such a one has been known for a long time.

As kobellite, Setterberg‡ in 1839 first described a mineral from the cobalt mines of Hvena, in Sweden, the composition§ of which he found to be:—

S	= (18·61)
Bi	= 28·37
Sb	= 9·38
Pb	= 40·74
Fe	= 2·02
Cu	= 0·88
	100·00

Deducting from this the copper with the equivalent quantities of iron and sulphur, the atomic ratio are as follows:—

S	= 0·5506		= 2·581
Bi	= 0·1351	0·2133	= 1·000
Sb	= 0·0782		
Pb	= 0·1966	0·2187	= 1·025
Fe	= 0·0221		

that is, they are identical with those calculated from my analysis.

Setterberg states distinctly that the iron of his mineral was dissolved in hydrochloric acid, and must therefore be considered as belonging to it; another slight difference in the composition of the minerals from the two localities is the replacement of about one-twelfth of the lead by silver in that from Ouray.

In 1862 Rammelsberg published an analysis of some material from the Hvena mine; he found:—

S	= 18·22
Bi	= 18·60
Sb	= 9·46
As	= 2·56
Pb	= 44·25
Fe	= 3·81
Cu	= 1·27
Co	= 0·68
	98·85

After deducting 5·61 per cent of (FeCo)AsS and 3·67 per cent of $CuFeS_2$, he arrives at the formula—

Pb_3BiSbS_6.

In his "Mineralchemie" (p. 100), he gives an analysis of so-called kobellite from another locality (the name of which is not mentioned), and from this deduces the same formula.

He does not prove, however, that the analysis by Setterberg is incorrect, and it is more than likely that the material examined by him consisted of a mineral different from Setterberg's.

There are numerous instances of the occurrence of two different sulpho salts of similar appearance in the same vein, and even upon the same piece.

The re-investigation of alaskaite by Kœnig* was caused by it having been mistaken for cosalite from the same mine.

The specific gravity determinations also show a slight discrepancy; Setterberg found 6·29—6·32, while Rammelsberg's determination gave 6·145. That of the Ouray occurrence is 6·334.

In view of all these facts, I feel myself justified in retaining the name of kobellite for the mineral of the formula:—

$$2(Pb,Ag_2,Cu_2,Fe)S, (Bi_{(\frac{2}{3})}Sb_{(\frac{1}{3})})S_3,$$

and would suggest that another name be given to that to which the name has hitherto been applied, namely,—

Pb_3SbBiS_6.

In concluding, I desire to propose the name of lillianite for a mineral from the Lillian mine in Leadville, Col., described several years ago jointly by my brother and myself as a variety of kobellite. It possesses the composition $3(PbAg_2)S$, Bi_2S_3, and represents the bismuth mineral corresponding to boulangerite.

II. *Analysis of Megabasite from Bonita Mountain, near Silverton, Col.*

More than three years ago I received from Colorado, among other specimens, one which was labelled "gœthite." Some qualitative tests that were then performed upon it proved that it consists essentially of tungstic acid and manganous oxide. The occurrence has become quite well known since, but, as far as I am aware, no quantitative analysis of the material has been published. I may therefore be permitted to put the following on record:—

Sp. gr. = 6·780.

WO_3	= 74·24
MnO	= 21·09
FeO	= 2·06
CuO	= 0·11
MgO	= trace
SiO_2	= 2·13
	99·63

* Chalcopyrite, when finely divided, is slightly acted upon by HCl.

† I have reason to believe that the antimony determinations I. and II. are a little too low.

‡ *Pogg. Ann.*, lv., 536.

§ Re-calculated with present atomic weights (Rammelsberg, *Mineralch.*, p. 100.

THE LUNDBERG CASE.†

By ELWYN WALLER, Ph.D.

SOME years ago (about 1880) Mr. Gustav Lundberg, agent for Messrs. Hoglund, of Sweden, contracted to supply to the Albany and Rensellaer Steel and Iron Co. a certain number of tons of Swedish pig-iron. In a letter appended to the contract was given the analysis of a sample of this iron (made in Sweden), and it was substantially agreed that the iron supplied should not be inferior in quality to that represented by the analysis. The iron was delivered, but the company claimed that it did not conform in quality to the contract, especially in the percentage of phosphorus. The result was a dispute as to payment, and consequently suit was brought. The case was tried about

* *Proc. Amer. Philos. Soc.*, 1885, 211.

† From the *School of Mines Quarterly*, Vol. x., No. 3, April, 1889.

Phosphorus.

Analyst.	Sample.	Grms. taken.	Method of analysis.	Furnace marks. NB GPH.	SBVE.	NB^{B} BK.
S. B. Sharples ..	a	—	A MM	0·02	0·041	0·0055
J. B. Mackintosh ..	b	2	N MM	trace	0·01	0·01
,, ..	,,	5	,,	0·032	0·032	0·025
A. H. Elliott	c	5	Cl MM	trace	trace	0
,, ...	,,	10	N MM	0·0307	0·0223	0·028
,, ...	,,	10	A MM*	0·025	0·0223	—
E. B. Hills	d	—	A MM	0·027	0·033	0·022
S. C. Eaton	,,	1	Eggertz	0·016	0·0039	0·0039
J. M. Sherrerd ..	e	6—8	N MM	—	0·038, 0·041, 0·040, 0·0395	—
P. W. Shimer . ..	,,	3—4	N MM	—	0·039, 0·039	—
A. S. Bertolet . ..	f	5	N MM	0·048	—	—
J. M. Sherrerd ..	,,	6—8	N MM	0·0528, 0·0544, 0·0508	—	—
—	—	—	—	0·0491, 0·0499	—	—
A. S. McCreath ..	g	5—10	A Cit	0·0458, 0·0463, 0·0444	0·0391, 0·0382, 0·0391	0·0452, 0·0458, 0·0441
,, ..	,,	5	Cl Cit	0·0447	—	—
J. M. Sherrerd . ..	,,	5—7	N MM	0·048, 0·0475, 0·047	0·0424, 0·0413, 0·0367	0·045, 0·046, 0·0437
A S. McCreath ..	h	5—10	A Cit	0·0463, 0·0469, 0·0455	—	—
J. M. Sherrerd . ..	,,	6—8	N MM	0·048, 0·0486, 0·0467	—	—
A. S. McCreath ..	i	5	A Cit	0·0464, 0·0463, 0·0474	—	—
A. A. Blair	,,	10	N Cit	0·043	—	—
W. O. Wuth	,,	5	N MM	0·047, 0·047	—	—
J. M. Sherrerd . ..	,,	5—7	N MM	0·0475, 0·0479, 0·0467	—	—
A. S. McCreath ..	j	5—10	A Cit	0·048, 0·0469	—	—
,, ..	,,	5	Cl Cit	0·0474	—	—
A. A. Blair	,,	5	N Cit	0·044	—	—
W. O. Wuth	,,	5	N MM	0·048, 0·048	—	—
J. M. Sherrerd . ..	,,	6—8	N MM	0·0493, 0·0475, 0·0479	—	—
A. S. McCreath ..	k	5—10	A Cit	0·0435	—	0·0402
—	,,	5	Cl Cit	0·0446	—	0·0407
W. O. Wuth	,,	5	N MM	0·046, 0·046	—	0·044, 0·0438
J. M. Sherrerd . ..	,,	5—7	N MM	0·0446, 0·0431	0·0363, 0·0355	0·0413, 0·0403
A. H. Sherrerd and D. W. Humphreys	l	5	N MM	0·0425, 0·0419	0·03520, 0·358	0·0425, 0·0413, 0·0430
T. M. Drown	,,	5—8	N MM	0·0445, 0·0422, 0·0441	0·0336, 0·0345, 0·0344	0·0420, 0·0405, 0·0414
S. A. Ford	,,	4—10	N Cit	0·0456, 0·048	0·0394, 0·0396	0·040, 0·041
W. O. Wuth	,,	5	N MM	0·048	0·038	0·047
T. H. Garrett	,,	3—4	N Cit	0·049, 0·052, 0·052	0·042, 0·039, 0·044	0·040, 0·046, 0·049
A. S. Bertolet	,,	5	N MM	0·046	0·044	0·050
J. M. Sherrerd . ..	,,	6—8	N MM	0·053, 0·0527	—	0·0468, 0·0503

* Second method, Cairns' "Quant. Anal.," p. 82.

a year after before a jury, decided, appealed, and a new trial ordered, which finally took place in 1887. Numerous analyses of the iron were made by different chemists in the country, and the trials brought out voluminous and interesting testimony as to methods of analysis, the discrepancies to be expected from different analysts, the difference between different pigs from the same furnace, &c. Some of the points relating more especially to the questions of analytical chemistry involved have been here collected from the stenographic notes on the case, which were kindly placed at my disposal for this purpose by Mr. Everett P. Wheeler, one of the counsel for Mr. Lundberg. The notes, however, in some few respects were not absolutely complete, so that a few omissions in the record have been unavoidable.

In the tables of results the sets of samples are designated by letters. In some cases borings were sent to the analysts; in many others, however, certain pigs of the iron were taken to their laboratories, and each analyst took his own borings, so that where two or more analysts are credited in the tables with having had the same sample, they frequently had only borings from the same pigs.

The iron was from three different furnaces, presumably running uniformly, and the pigs from each furnace were designated by a set of letters cast into each pig. The marks were respectively NB GPH, SBVE, and NB^{B} BK.

In the tables of results is incorporated a brief suggestion of the mode of analysis pursued.

Results for Phosphorus.

In the column headed Methods of Analysis the first letter indicates the solvent employed at the start. A signifies *aqua regia* or, at least, nitric acid with some addition of hydrochloric; N signifies nitric acid; and Cl chlorate of potash and hydrochloric acid. Succeeding these, MM indicates the use of the molybdate-magnesia method, and Cit the citric acid method. The methods will be more fully described later on.

Methods Used for the Determination of Phosphorus.

Amount Taken.—Most of the analysts used at least 5 grms. The amount, however, varied from one to ten.

Solution of the Iron.—The majority of the analysts seem to have used nitric acid alone, though in some cases it appeared that a little hydrochloric acid had been afterwards added, and in describing the method the witnesses had forgotten to mention it, as it was regarded by them as unimportant, the hydrochloric acid only being used occasionally to hasten the action. Three used *aqua regia* as their regular method. Messrs. Garrett, McCreath, and J. M. Sherrerd tried the use of other solvents than it had been their custom to use. No perceptible influence on the result ensued, though Dr. Wuth expressed a positive belief, founded on the observations of Stockmann (*Fres. Zeits.*, xvi., 172), that HCl could not be used in the solution of the iron without loss of phosphorus as PCl_3. On the other hand, several of the analysts declared, as the results of their own experience, that the use of some HCl

was admissible, all, of course, agreeing upon the necessity of the predominance of a strong oxidising agent.

Evaporation.—After effecting solution, evaporation to dryness necessarily followed, but in the heating of the evaporated mass to render the silica insoluble and to destroy carbonaceous material, the practice was very varied, both as to temperature and as to time. The widest difference was between heating for several hours (about ten) to 110° C. (Mackintosh), and heating for a short time to dull red heat (Wuth). Aside from these extremes the time varied from thirty minutes to three hours, the temperature from 120° to 165° C. Messrs. Blair and Wuth testified to dissolving in HCl after the first heating, and again evaporating to dryness.

To recover the small amount of iron, and possibly of phosphorus, which might have adhered to the silica, Dr. Drown ignited after filtering and treated with *aqua regia*; Messrs. Garrett and Blair expelled the silica by hydrofluoric acid, fused the residue with alkaline carbonate, and added the solution therefrom to the main solution. The other analysts did not testify to having taken any such precaution, and presumably in most cases it was omitted.

Further Treatment. — Beyond this point there was inevitably a divergence, according to the method to be pursued. Messrs. Ford, Garrett, Blair, and McCreath used the "citric acid method," or, as some called it, the "acetate method." The iron was reduced by alkaline sulphite, sulphuretted hydrogen passed through to remove arsenic if present, the solution filtered, boiled, and then a portion of the iron re-oxidised. For this purpose Messrs. Garrett and Blair used bromine ; Messrs. Ford and McCreath used potassium chlorate. Then, after neutralising with ammonia and adding alkaline acetate, basic ferric acetate containing the phosphorus was precipitated by boiling. The precipitate was dissolved in hydrochloric acid, and citric acid added, followed by magnesium mixture and ammonia.

Both of the Messrs. Sherrerd passed H_2S through the filtrate from the silica to remove arsenic if present, and then re-oxidised the whole of the iron. Messrs. Mackintosh and Elliott reduced the iron as above described, re-oxidised a portion with potassium permanganate, and precipitated as for the "citric acid method," but carried the precipitate through by the molybdate-magnesia method (Cairns' second method).

Molybdate Precipitation.—There was a substantial agreement on all sides as to the necessity for effecting the molybdate precipitation in presence of a predominance of nitric acid and nitrates; as to the permissibility of the presence of hydrochloric acid and chlorides there was some difference of opinion and practice. As to the amount of molybdate reagent used, the time the mixture was allowed to stand, and the temperature at which it stood, there was a great diversity of practice. Mr. Eaton (who used the Eggertz method by request of one of the counsel, and took but 1 grm. of the iron in accordance with Eggertz's directions*) used 10 c.c. only. 25 c.c. was used by some other analysts, and 100 c.c. by several others. The mixtures were usually allowed to stand for precipitation over night, though some prolonged the standing to twenty-four or even forty hours. The temperature employed was sometimes the ordinary temperature of the laboratory, sometimes about 40° C.

Dilute molybdate solution, dilute acidified ammonium nitrate, or dilute nitric acid were used in washing the precipitate.

Magnesium Precipitation.—In some cases the molybdate precipitation had been so managed that the ammonia used for solution left behind a small amount of iron, so that some of the analysts, as a regular custom, passed hydrochloric acid through the filter-paper, and then added a small amount of citric acid or of Rochelle salt before adding the magnesium mixture.

Messrs. Drown, Mackintosh, and J. M. Sherrerd testified to allowing the ammoniacal solution to stand for some time in order to allow any silica, &c., to separate and to be filtered off before adding the magnesium mixture.

The amounts of magnesium mixture used ranged from 2 c.c. to 25 c.c. From 10 to 20 c.c. were most frequently used.

So far as the testimony went, the magnesium mixture prepared with the chloride (Gooch's formula) was invariably used.

The time allowed for the deposition of the precipitate varied from two or three hours to twelve or fifteen. The most common practice appeared to be allowing it to stand over night. The addition of alcohol to the ammonia solution used for washing was mentioned by several as their usual habit.

Testing the Precipitate.—In most cases, after the ignition of the precipitate and weighing, it was dissolved in acid, and the insoluble silica, if present, filtered off and its weight deducted. Where provision had not been previously made for the removal of arsenic, the solution was tested with sulphuretted hydrogen.

Mr. A. H. Sherrerd, by his assistant, Mr. D. H. Humphreys, carried through a blank ordinary analysis, and deducted the amount so found from the weight of the precipitate obtained.

(To be continued).

* *Vide* Chemical News, ii., 227.

OBITUARY.

PROFESSOR VICTOR EGGERTZ.

We regret to announce the death of the late Professor Victor Eggertz at the age of 72, who died at Stockholm last week.

He had, since 1883, been at the head of the School of Mines in Sweden, first at Fahlun and then at Stockholm, until a few years ago, when he retired, and his place was filled by Professor Richard Akermann.

Professor Eggertz was the inventor of the so-called colouration-test for analysing carbon in iron and steel, which has done so much good to all steel-making processes. This test was introduced into England as far back as 1860, when Mr. C. P. Sandberg gave a translation of Professor Eggertz's methods, and published them in the Chemical News, and there are now hardly any steel works in the country which do not use this rapid method of ascertaining the hardness of steel almost immediately when made, thus enabling assortments in the control and regularity of the product; and with the immense production of Bessemer and Siemens steel now going on it is easily conceived what a practical value this method of carbon estimation has had upon the steel production of the country.

CORRESPONDENCE.

VERMILION OR VERMILLION?

To the Editor of the Chemical News.

Sir,—Though of no particular importance, I would like to know if your numerous readers can explain why vermilion is sometimes spelt with one *l* and sometimes with two. Authorities in this respect differ. Ordinarily in English books we have "vermilion," which is also found in "Skeats's Dictionary," and, being allied to, or derived from, *vermeil*, we should suppose this to be the right spelling. This form is found in Frankland and Japp's "Inorganic Chemistry," and Watts, in "Fownes' Chemistry," uses both forms, "vermillion" in

the index, and "vermilion" in the body of the work. And "vermillion" is found in "Wagner's Chemical Technology," in Roscoe and Schorlemmer's "Treatise," and in Henry Watts's "Dictionary of Chemistry."—I am, &c.

J. Tsawoo-White.

Rangoon College, July 30, 1889.

THE BRITISH ASSOCIATION.

To the Editor of the Chemical News.

Sir,—I shall be obliged by your announcing in the next number of your journal that, at the Newcastle Meeting of the British Association there will be a joint discussion, by Sections B and G, of a paper to be read in the latter Section by Sir I. Lowthian Bell, F.R.S., President of Section B, on "Blast Furnace Practice."—I am, &c.,

Edward Rigg,
Recorder, Section G.

9, Royal Mint, E.C.,
August 30, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Moniteur Scientifique, Quesneville.
June, 1889.

On Alloys.—Professor W. Chandler Roberts-Austen, F.R.S.—From the *Journal of the Society of Arts*.

Arsenic in the Household.—Dr. W. Stokes.—From the Chemical News.

On the Same Subject.—From the Chemical News.

Existence of a Volatile Alkaloid in Pepper.—W. Johnstone.—From the Chemical News.

On Bumping during Ebullition.—C. Tomlinson.—From the Chemical News.

Some Curious Properties of Metals and Alloys.—Prof. W. Chandler Roberts-Austen.—From the Chemical News.

Determination of Fat in Milk and Cream, &c.—W. Schmid.—This paper will be noticed under the *Zeitschrift f. Anal. Chemie*.

Experiments on the Fermentation of Galactose, Arabinose, Sorbose, and some other Sugars.—W. Stone and B. Tollens.—Noticed under *Liebig's Annalen*.

Industrial Review and Patents.—A selection of specifications of chemical patents. Among these we find Dr. G. Krüss's method for obtaining pure nickel from the nickel of commerce or from its salts. The object of the patent is to separate pure nickel from the element which the author has provisionally designated as *x*. This object is effected by treating the solutions of nickel salts with basic ammonium oxalate, by melting with an excess of caustic soda the concentrated solution after having eliminated the oxalic acid, by taking up in a mineral acid or acetic acid the hydroxide which remained undissolved in the treatment with melting alkali, and treating it in heat with caustic soda or with a soluble oxalate in presence of organic acids capable of preventing the precipitation of alumina by the fixed alkalies, and by treating the mixture of Ni and *x* or of their salts by a metal more electropositive than nickel in a state of fine division.

New Process for the Industrial Production and the Partial Synthesis of Cocaine.—C. Liebermann and F. Giesel.—This paper, which does not admit of useful abstraction, is taken from the Berlin *Berichte*.

Improvement in the Manufacture of Potassium Chlorate.—J. Hamill.—From the *Journal of the Society of Chemical Industry*.

Decomposition of Potassium Chlorate by Heat in Presence of Manganese Peroxide.—Herbert McLeod.—From the *Journal of the Chemical Society*.

Industrial Society of Mulhouse.—Meeting of February 13th.—M. Noelting read a report on the work of M. Wiss, entitled "Summary of Novel Hypotheses on Chemistry in Space."

M. Galland presented a report on a memoir by M. Camille Schoen on the fixation of basic colouring-matters by means of tungstic acid.

M. Noelting read, on behalf of C. Krohn, a paper on the ethylenic ethers of the three amidophenols and the colouring-matters thence derived.

M. Noelting mentioned that in conjunction with M. Schwartz he had obtained triquinolylmethane on treating paraleucaniline or pararosaniline with glycerin, sulphuric acid, and picric acid.

Session of March 13, 1889.

M. Noelting communicated some novel results obtained on studying the nitro- and amido-toluquinoleins. He also read some historical notes on aniline-black.

Session of April 10, 1889.

Horace Kœchlin read a paper on the fixation of the St. Denis red. He also mentions that he has obtained good results in bleaching by the use of oxygenated water and magnesia.

M. Weber, of Winterthur, fixes chrome mordants in the cold with zincate of soda.

The Progress of Dyeing during the Second Half of 1888.—Dr. Erdmann (*Chemische Industrie*).—This paper does not admit of useful abstraction.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xix., No. 9.

The Fixation of Nitrogen in Slow Oxidations.—M. Berthelot.—Already noticed.

Fraudulent Panification. The Use of Copper Sulphate and Alum in the Production of Bread.—M. Bruylants (*Académie Royale de Médicine de Belgique*.—The author mentions the use of sodium, magnesium, ammonium carbonates, and of lime-water as of little importance, that of soap (!) as very rare, and that of zinc and copper sulphates and of alum as objectionable, giving a distinct character to the fermentation.

Variable Causticity of Phenol According to its Solvents.—P. Carles.—When pure phenol is dissolved in pure glycerin or strong alcohol its caustic properties are much reduced, but they return if water is added to the mixture, even in small proportions.

New Method of Determining Lithia by Means of the Fluorides.—A. Carnot.—Already noticed.

The Active Principles of Panama Bark.—MM Bielkin, Kobert, and Pachorufoff.—The saponine of Panama bark, which has been mistaken for a unitary principle, is a mixture of a highly poisonous compound, sapotoxine, and of a carbohydrate named lactosine. There is also present quillajic acid, a second poisonous body, having the characters of a glucoside. This acid is proposed as a reagent for detecting albumen in urine if the liquid has been slightly acidulated with acetic acid.

Detection of Mercury in Animal Liquids.—Prof. Merget (*Soc. Pharm. de Bordeaux*).—The author's process consists of three operations: treatment with nitric acid, precipitation of the mercury by copper, and detection of the metal by the action of its vapours upon a test-paper prepared with ammmoniacal silver nitrate.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. i., No. 11.

Preliminary Note on the Reactions of Dimethylaniline in Presence of Aluminium Chloride.—H. Giraud.—On treating dimethylaniline with ferric chloride either alone or mixed with aluminium chloride, all the ferric chloride is reduced, but there are formed merely red pitchy matters from which only traces of methylbenzidine can be extracted. If dimethylaniline is heated in an atmosphere of dry oxygen with pure aluminium chloride there is a rapid absorption of oxygen and a very large quantity of methylbenzidine is obtained.

Action of Hydrochloric Acid upon the Solubility of Cuprous Chloride.—R. Engel.—From 0° to 17° the solubility of cuprous chloride in hydrochloric acid increases very slightly with the temperature. Above 17° the solubility of cuprous chloride becomes greater.

Action of Hydrochloric Acid upon the Solubility of Lead Chloride.—R. Engel.—The author gives his results in the form of a table.

On the Hydrochlorates of the Chlorides in General.—R. Engel.—All the known hydrochlorates of chlorides are hydrated, the minimum quantity of water being 2 mols. to 1 mol. of hydrochloric acid. When hydrochloric acid combines at one and the same temperature in multiple proportions with a chloride the quantity of water increases by 2 mols. for 1 additional mol. of acid. No hydrochlorate of a chloride is insoluble, and the solubility of every such hydrochlorate is greater than that of the corresponding chloride, the hydrochlorate of the cupric chloride forming the sole exception. The increased solubility of certain chlorides in presence of hydrochloric acid is due to the formation of a hydrochlorate of a chloride.

Supplementary Note on the Colouring-matters derived from the Tetrabenzilic Ether of Benzidine. Albert Colson.—The colouring-matters extracted from the tetrazo-derivative of oxybenzylic benzidine have such an affinity for cotton that aqueous solutions of these colours can be totally decolourised by the introduction of cotton-yarn.

Use of Potassium Permanganate to Detect the Impurities of Alcohols.—P. Cazeneuve.—Permanganate shows if alcohol contains impurities, but it does not indicate their nature if they are agreeable aromas appreciated by the *gourmet* or volatile products which may exert a poisonous action. It does not inform the consumer if he is buying a good or a hurtful cognac, but it is of use to the pharmacist and the manufacturer of liqueurs who require a chemically pure alcohol as the basis of their preparations.

The Rapidity of Transformation of Metaphosphoric Acid.—Paul Sabatier.—This memoir does not admit of useful abstraction.

Use of Coloured Gases in Photography.—M. Delaurier.—M. Lippmann's researches on producing photographs having just proportions of light remind the author of some fruitless attempts of his own to obtain photographs in their natural colours by making use of three glasses, red, yellow, and blue. In these experiments he found that light, on passing an orange glass, gave an equality of photogenic action for objects of whatsoever nature.

Vol. i., No. 12.

Certain Combinations and Reactions of Nitric Oxide and of Nitrogen Peroxide with Some Anhydrous Chlorides.—A. Besson.—Nitrogen dioxide combines directly with liberation of heat with anhydrous antimony pentachloride. If rise of temperature is avoided there is no escape of gas. There is formed a crystalline mass having the composition $2SbCl_5NO_2$. Bismuth trichloride, gently heated in a current of nitric oxide, combines directly, forming a crystalline body. Nitrogen peroxide, if dry, combines directly with anhydrous antimony pentachloride to form a crystalline solid, $3SbCl_5,2NO_4$. Nitrogen acts also upon antimony terchloride, bismuth chloride, aluminium chloride, and ferric chloride. Upon sulphur chloride nitrogen does not exert an oxidising action, as it does upon the selenium chlorides.

The Oxidation of Triphenylmethane.—MM. Hanriot and O. St. Pierre.—The authors have discovered that the triphenylmethane which they had used in their researches was not quite pure, having been obtained from a benzene containing a little toluene.

Action of Potassium upon Triphenylmethane.—MM. Hanriot and Saint-Pierre.—The reaction of potassium upon triphenylmethane is the first instance of the direct substitution of a metal for the hydrogen of a hydrocarbon. The authors find that it may be extended to fluorene, anthracene, and naphthalin.

Vol. ii., No. 1.

Chemical Composition of the Rock Salt of Roumania.—M. Istrati.—The rock-salt contains from 98·052 to 99·894 of actual sodium chloride. It sometimes contains gases, a mixture of non-saturated hydrocarbons, and of oxygen sufficient to cause slight explosion. The author has never detected any compound ammonias, and the odour and flavour of petroleum found in some of the beds are easily expelled by exposure to the air, or by heat.

Determination of Nitric Nitrogen by Means of Ferrous Sulphate.—M. Bailhache.—Already noticed.

Vol. ii., No. 2.

Fixation of Nitrogen by the Bare Arable Soil with or without the Co-operation of Leguminous Plants. M. Berthelot.

The Fixation of Nitrogen in Slow Oxidations.—M. Berthelot.

The Origin of Bronze and the Sceptre of Pepi I., King of Egypt.—M. Berthelot.

The Reactions between Chromic Acid and Oxygenated Water.—M. Berthelot.

Continuation of the Same (Parts II. and III.).—M. Berthelot.

Formation-heat of Hydrogen Antimonide.—MM. Berthelot and Petit.

Combustion-heat of Carbon in its Different States.—MM. Berthelot and Petit.

Researches on the Thionic Series, Nos. I., II., and III.—M. Berthelot.—All these papers have been already noticed.

Journal fur Praktische Chemie.
Vol. xxxix., Nos. 10 and 11, 1889.

Researches from the Laboratory of the University of Freiburg.—This series includes papers by C. Willgerodt and H. Salzmann on the halogen-substituted toluols and benzoic acids; by Ad. Claus and H. Kunath on the bromotoluylic acids; by Ad. Claus and Nils Davidson on the chloroparatoluylic acids; and by K. Elbs and O. Hoermann on diphenoltrichloraethan and paradioxystilbene.

Calorimetric Investigations.—F. Stohmann.—A memoir by the author in conjunction with Cl. Kleber and H. Langbein on the method of combustion of organic substances in oxygen under high pressure. The paper, which is very extensive, cannot be reproduced without the accompanying plate.

Researches from the Laboratory of Prof. Alex. Saytzeff at Kasan ("On the Action of Iodethyl and Zinc upon Paraldehyd," by Woldemar Wwedensky).—The results of this reaction prove that, although the secondary butylic alcohol is formed it is in such trifling quantities that its origin must be ascribed to acetaldehyd, which, under the conditions present, is formed from paraldehyd.

MISCELLANEOUS.

Tuson Fund.—At a meeting of the Committee, held at the Royal Veterinary College on May 13, 1889, the accounts having been previously audited by Professors Attfield and Axe, the hon. secretaries were able to report that the total receipts amounted to £933 2s. 10d. Since that date a further sum of £60 17s. 9d. has been received, making a grand total of £994 0s. 7d. The balance sheet presented to the Committee showed that £96 10s. had been paid either directly to or on account of Mrs. Tuson, and that £17 10s. 1d. had been expended on printing, stationery, &c., leaving an available balance to date of £819 2s. 9d.; this, with the £60 17s. 9d. since received, gives a total of £880 0s. 6d. to be dealt with. The Committee decided that £750 should be expended in the purchase of an annuity for Mrs. Tuson, and that the balance should be expended for her benefit in such a manner as the hon. secretaries might think best. The hon. secretaries are now pleased to report that an annuity of £63 15s. has been bought for Mrs. Tuson in the Prudential Assurance Company, and, as authorised by the Committee, they have expended a further sum on her account of £56 0s. 1d., leaving a balance in hand of £74 0s. 5d. There still remains to be paid a small account for printing and postage, which will reduce this to about £70; this it is proposed to hand over to Mrs. Tuson. The hon. secretaries are requested by Mrs. Tuson to take this opportunity of offering to all those who have so kindly come to her assistance her most sincere and heartfelt thanks. — C. W. HEATON, RICHARD A. N. POWYS, Hon. Secretaries,

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Zinc Chloride—Can any reader tell me the addresses of the principal makers of this substance, its present market value, and if it is used *largely* in any manufacturing operation?—C. H. E.

Thermal and Electrical Units.—Can any reader direct me to a book giving particulars of the heats developed or required to effect certain reactions in chemistry, *e.g.*, the heat developed when Na_2 combines with O to form Na_2O, and the heat required to effect the separation again of the same bodies? A complete article upon the subject is what I want to find. I should also be glad of any information upon the best treatise upon electrical units and measurements, and the amount of electrical force required to effect electrical decompositons.—W. G. H.

TO CORRESPONDENTS.

Analyst.—Consult Dr. Lunge's books on the subject.

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THE CHEMICAL NEWS.

Vol. LX. No. 1555.

BRITISH ASSOCIATION FOR THE ADVANCEMENT OF SCIENCE.

Newcastle-upon-Tyne, 1889.

INAUGURAL ADDRESS OF THE PRESIDENT,

Professor W. H. Flower,
C.B., LL.D., F.R.S., F.R.C.S., Pres.Z.S., F.L.S., F.G.S.

It is twenty-six years since this Association met in Newcastle-upon-Tyne. It had then the advantage of being presided over by one of the most distinguished and popular of your fellow-townsmen.

Considering the age usually attained by those upon whom the honour of the presidency falls, and the length of time which elapses before the Association repeats its visit, it must have rarely happened that any one who has held the office is spared, not only to be present at another meeting in the town in which he has presided, but also to take such an active part in securing its success, and to extend such a hospitable welcome to his successor, as Lord Armstrong has done upon the present occasion.

The address which was delivered at that meeting must have been full of interest to the great majority of those present. It treated of many subjects more or less familiar and important to the dwellers in this part of the world, and it treated them with the hand of a master, a combination which always secures the attention of an audience.

When it came to my knowledge that in the selection of the President for this meeting the choice had fallen upon me, I was filled with apprehension. There was nothing in my previous occupations or studies from which I felt that I could evolve anything in special sympathy with what is universally recognised as the prevailing genius of this district. I was, however, somewhat reassured when reminded that in the regular rotation by which the equal representation in the presidential office of the different branches of science included in the Association is secured, the turn had come round for some one connected with biological subjects to occupy the chair, which during the past seven years has been filled with such distinction by engineers, chemists, physicists, mathematicians, and geologists. I was also reminded that the Association, though of necessity holding its meeting in some definite locality, was by no means local in its character, but that its sphere was co-extensive, not with the United Kingdom only, but with the whole of the British Dominions, and that our proceedings are followed with interest wherever our language is understood—I may say, throughout the civilised world. Furthermore, although its great manufacturing industries, the eminence of its citizens for their skill and intelligence in the practical application of mechanical sciences, and the interesting and important geological features of its vicinity, have conferred such fame on Newcastle as almost to have overshadowed its other claims to distinction in connection with science, this neighbourhood is also associated with Bewick, with Johnson, with Alder, Embleton, Hutton, Atthey, Norman, the two Hancocks, the two Bradys, and other names honoured in the annals of biology; it has long maintained a school of medicine of great repute; and there has lately been established here a natural history museum, which in some of its features is a model for institutions of the kind, and which, I trust, will be a means of encouraging in this town some of the objects the Association was designed to promote.

There can be no doubt that among the various methods by which the aims of the British Association (as expressed in its full title, the *advancement of science*) may be brought about, the collection and preservation of objects available for examination, study, and reference—in fact, the formation of what are now called "museums"—is one of very great practical importance; so much so, indeed, that it seems to me one to the consideration of which it is desirable to devote some time upon such an occasion as this. It is a subject still little understood, though, fortunately, beginning to attract attention. It has already been brought before the notice of the Association, both in presidential and sectional addresses. A committee of our members is at the present time engaged in collecting evidence upon it, and has issued some valuable reports. During the present year an association of curators and others interested in museums has been founded for the purpose of interchange of ideas upon the organisation and management of these institutions. It is a subject, moreover, if I may be allowed to mention a personal reason for bringing it forward this evening, which has more than any other occupied my time and my attention almost from the earliest period of my recollection, and I think you will agree with the opinion of one of my distinguished predecessors in this chair, "that the holder of this office will generally do better by giving utterance to what has already become part of his own thought than by gathering matter outside of its habitual range for the special occasion. For," continued Mr. Spottiswoode, "the interest (if any) of an address consists not so much in the multitude of things therein brought forward as in the individuality of the mode in which they are treated."

The first recorded institution which bore the name of museum, or temple, or haunt of the Muses, was that founded by Ptolemy Soter at Alexandria about 300 B.C.; but this was not a museum in our sense of the word, but rather, in accordance with its etymology, a place appropriated to the cultivation of learning, or which was frequented by a society or academy of learned men devoting themselves to philosophical studies and the improvement of knowledge.

Although certain great monarchs, as Solomon of Jerusalem and Augustus of Rome, displayed their taste and their magnificence by assembling together in their palaces curious objects brought from distant parts of the world—although it is said that the liberality of Philip and Alexander supplied Aristotle with abundant materials for his researches—of the existence of any permanent or public collections of natural objects among the ancients there is no record. Perhaps the nearest approach to such collections may be found in the preservation of remarkable specimens, sometimes associated with superstitious veneration, sometimes with strange legendary stories, in the buildings devoted to religious worship. The skins of the gorillas brought by the navigator Hanno from the West Coast of Africa, and hung up in the temple at Carthage, afford a well-known instance.

With the revival of learning in the Middle Ages, the collecting instinct, inborn in so many persons of various nations and periods of history, but so long in complete abeyance, sprang into existence with considerable vigour, and a museum, now meaning a collection of miscellaneous objects, antiquities, as well as natural curiosities, often associated with a gallery of sculpture and painting, became a fashionable appendage to the establishment of many wealthy persons of superior culture.

All the earliest collections, comparable to what we call museums, were formed by and maintained at the expense of private individuals; sometimes physicians, whose studies naturally led them to a taste for biological science; often great merchant princes, whose trading connections afforded opportunities for bringing together things that were considered curious from foreign lands; or ruling monarchs in their private capacity. In every case they were maintained mainly for the gratification of the possessor or his personal friends, and rarely, if ever,

associated with any systematic teaching or public benefit.

One of the earliest known printed catalogues of such a museum is that of Samuel Quickelberg, a physician of Amsterdam, published in 1565 in Munich. In the same year Conrad Gesner published a catalogue of the collection of Johann Kentmann, a physician of Torgau in Saxony, consisting of about 1600 objects, chiefly minerals, shells, and marine animals. Very soon afterwards we find the Emperor Rudolph II. of Germany busily accumulating treasures which constituted the foundations of the present magnificent museums by which the Austrian capital is distinguished.

In England the earliest important collectors of miscellaneous objects were the two John Tradescants, father and son, the latter of whom published, in 1656, a little work called "Musæum Tradescantianum; or, a Collection of Rarities Preserved at South Lambeth, neer London." The wonderful variety and incongruous juxtaposition of the objects contained in this collection make the catalogue very amusing reading. Under the first division, devoted to "Some Kindes of Birds, their Egges, Beaks, Feathers, Clawes, and Spurres," we find "Divers sorts of Egges from Turkie, one given for a Dragon's Egge;" "Easter Egges of the Patriarch of Jerusalem;" "Two Feathers of the Phœnix Tayle;" "The Claw of the bird Rock, who, as Authors report, is able to trusse an Elephant." Among "whole birds" is the famous "Dodar from the Island Mauritius; it is not able to flie, being so big." This is the identical specimen, the head and foot of which has passed through the Ashmolean into the University Museum of Oxford; but we know not what has become of the claw of the Rock, the Phœnix tayle, and the Dragon's egg. Time does not allow me to mention the wonderful things which occur under the head of "Garments, Vestures, Habits, and Ornaments," or the "Mechanick, Artificial Workes in Carvings, Turnings, Sowings, and Paintings," from Edward the Confessor's knit gloves, and the famous "Pohatan, King of Virginia's habit, all embroidered with shells or Roanoke," also still at Oxford, and lately figured and described by Mr. E. B. Tylor, to the "Cherry-stone, upon one side S. George and the Dragon, perfectly cut, and on the other side eighty-eight Emperours' faces;" or the other "cherry-stone, holding ten dozen of tortois-shell combs made by Edward Gibbons." But before leaving these private collections I cannot forbear mentioning, as an example of the great aid they often were in advancing science, the indebtedness of Linnæus in his early studies to the valuable zoological museums, which it was one of the ruling passions of several kings and queens of Sweden to bring together.

Upon the association of individuals together into societies to promote the advancement of knowledge, these bodies in their corporate capacity frequently made the formation of a museum part of their function. The earliest instance of this in our country was the museum of the Royal Society in Crane Court, of which an illustrated catalogue was published by Dr. Grew in 1681.

The idea that the maintenance of a museum was a portion of the public duty of the State or of any municipal institution had, however, nowhere entered into the mind of man at the beginning of the last century. Even the great teaching bodies, the Universities, were slow in acquiring collections; but it must be recollected that the subjects considered most essential to the education they then professed to give were not those which needed illustration from the objects which can be brought together in a museum. The Italian Universities, where anatomy was taught as a science earlier and more thoroughly than anywhere else in Europe, soon found the desirability of keeping collections of preserved specimens, and the art of preparing them attained a high degree of excellence at Padua and Bologna two centuries ago. But these were generally the private property of the professors, as were nearly all the collections used to illustrate the teaching of anatomy and pathology in our country within the memory of many now living.

Notwithstanding the multiplication of public museums during the present century, and the greater resources and advantages which many of these possess, which private collectors cannot command, the spirit of accumulation in individuals has happily not passed away, although usually directed into rather different channels than formerly. The general museums or miscellaneous collections of old are now left to governments and institutions which afford greater guarantee of their permanence and public utility, while admirable service is done to science by those private persons with leisure and means who, devoting themselves to some special subject, amass the materials by which its study can be pursued in detail either by themselves or by those they know to be qualified to do so; which collections, if they fulfil their most appropriate destiny, ultimately become incorporated, by gift or purchase, in one or other of the public museums, and then serve as permanent factors in the education of the nation, or rather of the world.

It would be passing beyond the limits of time allotted to this address, indeed going beyond the scope of the Association, if I were to speak of many of the subjects which have pre-eminently exercised the faculties of the collector and formed the materials of which museums are constructed. The various methods by which the mind of man has been able to reproduce the forms of natural objects or to give expression to the images created by his own fancy, from the rudest scratchings of a savage on a bone, or the simplest arrangement of lines employed in ornamenting the roughest piece of pottery, up to the most lovely combinations of form and colour hitherto attained in sculpture or in painting, or in works in metal or in clay, depend altogether on museums for their preservation, for our knowledge of their condition and history in the past, and for the lessons which they can convey for the future.

Apart from the delight which the contemplation of the noblest expressions of art must produce in all cultivated minds, apart also from the curiosity and interest that must be excited by all the less successfully executed attempts to produce similar results, as materials for constructing the true history of the life of man, at different stages of civilisation, in different circumstance of living, and in divers regions of the earth, such collections are absolutely invaluable.

But I must pass them by in order to dwell more in detail upon those which specially concern the advancement of the subjects which come under the notice of this Association—museums devoted to the so-called "natural history" sciences, although much which will be said of them will doubtless be more or less applicable to museums in general.

The terms "*natural history*" and "*naturalist*" have become deeply rooted in our language, but without any very definite conception of their meaning or the scope of their application. Originally applied to the study of all the phenomena of the universe which are independent of the agency of man, natural history has gradually narrowed down in most people's minds, in consequence of the invention of convenient and generally understood and accepted terms for some of its various subdivisions, as astronomy, chemistry, geology, &c., into that portion of the subject which treats of the history of creatures endowed with life, for which, until lately, no special name had been invented. Even from this limitation botany was gradually dissassociating itself in many quarters, and a "naturalist" and a "zoologist" have nearly become, however irrationally, synonymous terms. The happy introduction and general acceptance of the word "biology," notwithstanding the objections raised to its etymological signification, have re-united the study of organisms distinguished by the possession of the living principle, and practically eliminated the now vague and indefinite term "natural history" from scientific terminology. As, how-

ever, it is certain to maintain its hold in popular language, I would venture to suggest the desirability of restoring it to its original and really definite signification, contrasting it with the history of man and of his works, and of the changes which have been wrought in the universe by his intervention.

It was in this sense that, when the rapid growth of the miscellaneous collections in the British Museum at Bloomsbury (the expansion of Sir Hans Sloane's accumulation in the old Manor House at Chelsea) was thought to render a division necessary, the line of severance was effected at the junction of what was natural and what was artificial; the former, including the products of what are commonly called "natural" forces, unaffected by man's handiwork or the impress of his mind. The departments which took cognisance of these were termed the "Natural History Departments," and the new building to which they were removed the "Natural History Museum."

It may be worth while to spend a few moments upon the consideration of the value of this division, as it is one which concerns the arrangement and administration of the majority of museums.

Though there is very much to be said for it, the objection has been raised that it cuts man himself in two. The illustrations of man's bodily structure are undoubtedly subjects for the zoologist. The subtile gradations of form, proportion, and colour which distinguish the different races of men, can only be appreciated by one with the education of an anatomist, and whose eye has been trained to estimate the value of such characters in discriminating the variations of animal forms. The subjects for comparison required for this branch of research must therefore be looked for in the zoological collections.

But the comparatively new science of "anthropology" embraces not only man's physical structure; it includes his mental development, his manners, customs, traditions, and languages. The illustrations of his works of art, domestic utensils, and weapons of war are essential parts of its study. In fact it is impossible to say where it ends. It includes all that man is or ever has been, all that he has ever done. No definite line can be drawn between the rudest flint weapon and the most exquisitely finished instrument of destruction which has ever been turned out from the manufactory at Elswick, between the rough representation of a mammoth, carved by one of its contemporary men on a portion of its own tusk, and the most admirable production of a Landseer. An anthropological collection, to be logical, must include all that is in not only the old British Museum, but the South Kensington Museum and the National Gallery. The notion of an anthropology which considers savages and prehistoric people as apart from the rest of mankind may, in the limitations of human powers, have certain conveniences, but it is utterly unscientific and loses sight of the great value of the study in tracing the gradual growth of our complex systems and customs from the primitive ways of our progenitors.

On the other hand, the division first indicated is as perfectly definite, logical, and scientific as any such division can be. That there are many inconveniences attending wide local disjunctions of the collections containing subjects so distinct yet so nearly allied as physical and psychical anthropology must be fully admitted; but these could only have been overcome by embracing in one grand institution the various national collections illustrating the different branches of science and art, placed in such order and juxtaposition that their mutual relations might be apparent, and the resources of each might be brought to bear upon the elucidation of all the others—an ideal institution, such as the world has not yet seen, but into which the old British Museum might at one time have been developed.

A purely "Natural History Museum" will then embrace a collection of objects illustrating the natural productions of the earth, and in its widest and truest sense should include, as far as they can be illustrated by museum specimens, all the sciences which deal with natural phenomena. It has only been the difficulties, real or imaginary, in illustrating them which have excluded such subjects as astronomy, physics, chemistry, and physiology from occupying departments in our National Natural History Museum, while allowing the introduction of their sister sciences, mineralogy, geology, botany, and zoology.

Though the experimental sciences and those which deal with the laws which govern the universe, rather than with the materials of which it is composed, have not hitherto greatly called forth the collector's instinct, or depended upon museums for their illustration, yet the great advantages of collections of the various instruments by means of which these sciences are pursued, and of examples of the methods by which they are taught, are yearly becoming more manifest. Museums of scientific apparatus now form portions of every well-equipped educational establishment, and under the auspices of the Science and Art Department at South Kensington a national collection illustrating those branches of natural history science which have escaped recognition in the British Museum is assuming a magnitude and importance which brings the question of properly housing and displaying it urgently to the front.

Anomalies such as these are certain to occur in the present almost infantile though rapidly progressive state of science. It may be taken for granted that no scientific institution of any complexity of organisation can be, except at the moment of its birth, abreast of the most modern views of the subject, especially in the dividing lines between, and the proportional representation of, the various branches of knowledge which it includes.

The necessity for subdivisions in the study of science is continually becoming more apparent as the knowledge of the details of each subject multiplies without corresponding increase in the power of the human mind to grasp and deal with them, and the dividing lines not only become sharper, but as knowledge advances they frequently require revision. It might be supposed that such revision would adjust itself to the direction taken by the natural development of the relations of the different branches of science, and the truer conceptions entertained of such relations. But this is not always so. Artificial barriers are continually being raised to keep these dividing lines in the direction in which they have once started. Difficulties of re-adjustment arise not only from the mechanical obstacles caused by the size and arrangements of the buildings and facilities for the allocation of various kinds of collections, but still more from the numerous personal interests which grow up and wind their meshes around such institutions. Professorships and curatorships of this or that division of science are founded and endowed, and their holders are usually tenacious either of encroachment upon or of any wide enlargement of the boundaries of the subject they have undertaken to teach or to illustrate; and in this way, more than any other, passing phases of scientific knowledge have become crystallised or fossilised in institutions where they might least have been expected. I may instance many European universities and great museums in which zoology and comparative anatomy are still held to be distinct subjects taught by different professors, and where, in consequence of the division of the collections under their charge, the skin of an animal, illustrating its zoology, and its skeleton and teeth, illustrating its anatomy, must be looked for in different and perhaps remotely placed buildings.

For the perpetuation of the unfortunate separation of palæontology from biology, which is so clearly a survival of an ancient condition of scientific culture, and for the maintenance in its integrity of the heterogeneous compound of sciences which we now call "geology," the faulty organisation of our museums is in a great measure responsible. The more their re-arrangement can be made to overstep and break down the abrupt line of

demarcation which is still almost universally drawn between beings which live now and those which have lived in past times, so deeply rooted in the popular mind and so hard to eradicate even in that of the scientific student, and the better it will be for the progress of sound biological knowledge.

But it is not of the removal of such great anomalies and inconsistencies which, when they have once grown up, require heroic methods to set them right, but rather of certain minor defects in the organisation of almost all existing museums which are well within the capacity of comparatively modest administrative means to remedy, that I have now to speak.

That great improvements have been lately effected in many respects in some of the museums in this country, on the Continent, and especially in America, no one can deny. The subject, as I have already indicated, is, happily, exciting the attention of those who have the direction of them, and even awakening interest in the mind of the general public. It is in the hope of in some measure helping on or guiding this movement that I have ventured on the remarks which follow.

The first consideration in establishing a museum, large or small, either in a town, institution, society, or school, is that it should have some definite object or purpose to fulfil; and the next is that means should be forthcoming not only to establish but also to maintain the museum in a suitable manner to fulfil that purpose. Some persons are enthusiastic enough to think that a museum is in itself so good an object that they have only to provide a building and cases and a certain number of specimens, no matter exactly what, to fill them and then the thing is done; whereas the truth is the work is only then begun. What a museum really depends upon for its success and usefulness is not its building, not its cases, not even its specimens, but its curator. He and his staff are the life and soul of the institution, upon whom its whole value depends; and yet in many—I may say most of our museums—they are the last to be thought of. The care, the preservation, the naming of the speciments are either left to voluntary effort—excellent often for special collections and for a limited time, but never to be depended on as a permanent arrangement—or a grievously undersalaried and consequently uneducated official is expected to keep in order, to clean, dust, arrange, name, and display in a manner which will contribute to the advancement of scientific knowledge, collections ranging in extent over almost every branch of human learning, from the contents of an ancient British barrow to the last discovered bird of paradise from New Guinea.

Valuable specimens not unfrequently find their way into museums thus managed. Their public-spirited owners fondly imagine that they will be preserved and made of use to the world if once given to such an institution. Their fate is, unfortunately, far otherwise. Dirty, neglected, without label, their identity lost, they are often finally devoured by insects or cleared away to make room on the crowded shelves for the new donation of some fresh patron of the institution. It would be far better that such museums should never be founded. They are traps into which precious—sometimes priceless—objects fall only to be destroyed; and what, is still worse, they bring discredit on all similar institutions, make the very name of museum a byword and a reproach, hindering instead of advancing the recognition of their value as agents in the great educational movement of the age.

A museum is like a living organism—it requires continual and tender care, it must grow or it will perish; and the cost and labour required to maintain it in a state of vitality is not yet by any means fully realised or provided for, either in our great national establishments or in our smaller local institutions.

Often as it has been said, it cannot be too often repeated, that the real objects of forming collections, of whatever kind (apart, of course, from the mere pleasure of acquisition—sometimes the only motive of private collectors), and which, although in very different degrees, and often without being recognised, underlie the organisation of all museums, are two, which are quite distinct, and sometimes even conflicting. The first is to advance or increase the knowledge of some given subject. This is generally the motive of the individual collector, whose experience shows him the vast assistance in forming definite ideas in any line of research in which he may be occupied that may be derived from having the materials for its study at his own command, to hold and to handle, to examine and compare, to take up and lay aside whenever the favourable moment to do so occurs. But unless his subject is a very limited one, or his means the reverse, he soon finds the necessity of consulting collections based on a larger scale than his own. Very few people have any idea of the multiplicity of specimens required for the purpose of working out many of the simplest problems concerning the life-history of animals or plants. The naturalist has frequently to ransack all the museums, both public and private, of Europe and America in the endeavour to compose a monograph of a single common genus, or even species, that shall include all questions of its variation, changes in different seasons, and under different climates and conditions of existence, and the distribution in space and time of all its modifications. He often has to confess at the end that he has been baffled in his research for want of the requisite materials for such an undertaking. Of course this ought not to be, and the time will come when it will not be, but that time is very far off yet.

We all know the old saying that the craving for riches grows as the wealth itself increases. Something similar is true of scientific collections brought together for the purpose of advancing knowledge. The larger they are the more their deficiencies seem to become conspicuous; the more desirous we are to fill up the gaps which provokingly interfere with our extracting from them the complete story they have to tell.

Such collections are, however, only for the advanced student, the man who has already become acquainted with the elements of his science, and is in a position, by his knowledge, by his training, and by his observing and reasoning capacity, to take advantage of such material to carry on the subject to a point beyond that at which he takes it up.

But there is another and a far larger class to whom museums are or should be a powerful means of aid in acquiring knowledge. Among such those who are commencing more serious studies may be included; but I especially refer to the much more numerous class, and one which it may be hoped will year by year bear a greater relative proportion to the general population of the country, who, without having the time, the opportunities, or the abilities to make a profound study of any branch of science, yet take a general interest in its progress, and wish to possess some knowledge of the world around them and of the principal facts ascertained with regard to it, or at least some portions of it. For such persons museums may be, when well organised and arranged, of benefit to a degree that at present can scarcely be realised.

To diffuse knowledge among persons of this class is the second of the two purposes of museums of which I have spoken.

I believe that the main cause of what may be fairly termed the failure of the majority of museums—especially museums of natural history—to perform the functions that might be legitimately expected of them is that they nearly always confound together the two distinct objects which they may fulfil, and by attempting to combine both in the same exhibition practically accomplish neither.

In accordance with which of those two objects, which may be briefly called *research* and *instruction*, is the main end of the museum, so should the whole be primarily arranged; and in accordance with the object for which each specimen is required, so should it be treated.

The specimens kept for research, for advancement of

knowledge, for careful investigations in structure and development, or for showing the minute distinctions which must be studied in working out the problems connected with variations of species according to age, sex, season, or locality; for fixing the limits of geographical distribution, or determining the range in geological time, must be not only exceedingly numerous (so numerous, indeed, that it is almost impossible to put a limit on what may be required for such purposes), but they must also be kept under such conditions so as to admit of ready and close examination and comparison.

If the whole of the specimens really required for enlarging the boundaries of zoological or botanical science were to be displayed in such a manner that each one could be distinctly seen by any visitor sauntering through the public galleries of a museum, the vastness and expense of the institution would be out of all proportion to its utility; the specimens themselves would be quite inaccessible to the examination of all those capable of deriving instruction from them, and, owing to the injurious effects of continued exposure to light upon the greater number of preserved natural objects, would ultimately lose a large part of their permanent value. Collections of this kind must, in fact, be treated as the books in a library, and be used only for consultation and reference by those who are able to read and appreciate their contents. To demand, as has been ignorantly done, that all the specimens belonging to our national museums, for instance, should be displayed in cases in the public galleries, would be equivalent to asking that every book in a library, instead of being shut up and arranged on shelves for consultation when required, should have every single page framed and glazed and hung on the walls, so that the humblest visitor as he passes along the galleries has only to open his eyes and revel in the wealth of literature of all ages and all countries, without so much as applying to a custodian to open a case. Such an arrangement is perfectly conceivable. The idea from some points of view is magnificent, almost sublime. But imagine the space required for such an arrangement of the national library of books, or, indeed, of any of the smallest local libraries; imagine the inconvenience to the real student, the disadvantages which he would be under in reading the pages of any work fixed in an immovable position beneath a glass case; think of the enormous distances he would often have to traverse to compare a reference or verify a quotation, and the idea of sublimity soon gives place to its usual antithesis. The attempt to display every bird, every insect, shell, or plant which is or ought to be in any of our great museums of reference would produce an exactly similar result.

In the arrangement of collections designed for research, which, of course, will contain all those precious specimens called "types," which must be appealed to through all time to determine the species to which a name was originally given, the principal points to be aimed at are—the preservation of the objects from all influences deleterious to them, especially dust, light, and damp; their absolutely correct identification, and record of every circumstance that need be known of their history; their classification and storage in such a manner that each one can be found without difficulty or loss of time; and, both on account of expense as well as convenience of access, they should be made to occupy as small a space as is compatible with these requirements. They should be kept in rooms provided with suitable tables and good light for their examination, and within reach of the necessary books of reference on the particular subjects which the specimens illustrate. Furthermore, the rooms should be so situated that the officers of the museum, without too great hindrance to their own work, can be at hand for occasional assistance and supervision of the student, and if collections of research and exhibited specimens are contained in one building, it is obvious that the closer the contiguity in which those of any particular group are placed the greater will be the convenience both of students and curators, for in very few establishments will it be possible to form each series on such a scale as to be entirely independent of the other.

On the other hand, in a collection arranged for the instruction of the general visitor, the conditions under which the specimens are kept should be totally different. In the first place, their numbers must be strictly limited, according to the nature of the subject to be illustrated and the space available. None must be placed too high or too low for ready examination. There must be no crowding of specimens one behind the other, every one being perfectly and distinctly seen, and with a clear space around it. Imagine a picture gallery with half the pictures on the walls partially or entirely concealed by others hung in front of them; the idea seems preposterous, and yet this is the approved arrangement of specimens in most public museums. If an object is worth putting into a gallery at all it is worth such a position as will enable it to be seen. Every specimen exhibited should be good of its kind, and all available skill and care should be spent upon its preservation and rendering it capable of teaching the lesson it is intended to convey. And here I cannot refrain from saying a word upon the sadly neglected art of taxidermy, which continues to fill the cases of most of our museums with wretched and repulsive caricatures of mammals and birds, out of all natural proportions, shrunken here and bloated there, and in attitudes absolutely impossible for the creature to have assumed while alive. Happily there may be seen occasionally, especially were amateurs of artistic taste and good knowledge of natural history have devoted themselves to the subject, examples enough—and you are fortunate in possessing them in Newcastle—to show that an animal can be converted after death, by a proper application of taxidermy, into a real life-like representation of the original, perfect in form, proportions, and attitude, and almost, if not quite, as valuable for conveying information on these points as the living creature itself. The fact is that taxidermy is an art resembling that of the painter or rather the sculptor; it requires natural genius as well as great cultivation, and it can never be permanently improved until we have abandoned the present conventional low standard and low payment for "bird-stuffing," which is utterly inadequate to induce any man of capacity to devote himself to it as a profession.

To return from this digression, every specimen exhibited should have its definite purpose, and no absolute duplicate should on any account be permitted. Above all, the purpose for which each specimen is exhibited, and the main lesson to be derived from it, must be distinctly indicated by the labels affixed, both as headings of the various divisions of the series, and to the individual specimens. A well-arranged educational museum has been defined as a collection of instructive labels illustrated by well-selected specimens.

What is, or should be, the order of events in arranging a portion of a public museum? Not, certainly, as too often happens now, bringing a number of specimens together almost by haphazard, and cramming them as closely as possible in a case far too small to hold them, and with little reference to their order or to the possibility of their being distinctly seen. First, as I said before, you must have your curator. He must carefully consider the object of the museum, the class and capacities of the persons for whose instruction it is founded, and the space available to carry out this object. He will then divide the subject to be illustrated into groups, and consider their relative proportions, according to which he will plan out the space. Large labels will next be prepared for the principal headings, as the chapters of a book, and smaller ones for the various sub-divisions. Certain propositions to be illustrated, either in the structure, classification, geographical distribution, geological position, habits, or evolution of the subjects dealt with, will be laid down and reduced to definite and concise language. Lastly will

come the illustrative specimens, each of which as procured and prepared will fall into its appropriate place. As it is not always easy to obtain these at the time that they are wanted, gaps will often have to be left, but these, if properly utilised by drawings or labels, may be made nearly as useful as if occupied by the actual specimens.

A public exhibition which is intended to be instructive and interesting must never be crowded. There is, indeed, no reason why it ever should be. Every such exhibition whether on a large or small scale, can only contain a representative series of specimens, selected with a view to the needs of the particular class of persons who are likely to visit the gallery, and the number of specimens exhibited should be adapted to the space available. There is, therefore, rarely any excuse for filling it up in such a manner as to interfere with the full view of every specimen shown. A crowded gallery, except in some very exceptional circumstances, at once condemns the curator, as the remedy is generally in his own hands. In order to avoid it he has nothing to do but sternly to eliminate all the less important specimens. If any of these possess features of historical or scientific interest demanding their permanent preservation, they should be kept in the reserve collections; if otherwise, they should not be kept at all.

The ideal public museums of the future will, however, require far more exhibition space than has hitherto been allowed; for though the number of specimens shown may be fewer than is often thought necessary now, each will require more room if the conditions above described are carried out, and especially if it is thought desirable to show it in such a manner as to enable the visitor to realise something of the wonderful complexity of the adaptations which bring each species into harmonious relation with its surrounding conditions. Artistic reproductions of natural environments, illustrations of protective resemblances, or of special modes of life, all require much room for their display. This method of exhibition, wherever faithfully carried out, is, however, proving both instructive and attractive, and will doubtless be greatly extended.

Guide-books and catalogues are useful adjuncts, as being adapted to convey fuller information than labels, and as they can be taken away for study during the intervals of visits to the museum, but they can never supersede the use of labels. Anyone who is in the habit of visiting picture galleries where the names of the artists and the subject are affixed to the frame, and others in which the information has in each case to be sought by reference to a catalogue, must appreciate the vast superiority in comfort and time-saving of the former plan.

Acting upon such principles as these, every public gallery of a museum, whether the splendid saloon of a national institution or the humble room containing the local collection of a village club, can be made a centre of instruction, and will offer interests and attractions which will be looked for in vain in the majority of such institutions at the present time.

One of the best illustrations of the different treatment of collections intended for research or advancement of knowledge, and for popular instruction or diffusion of knowledge, is now to be seen in Kew Gardens, where the admirably constructed and arranged herbarium answers the first purpose, and the public museums of economic botany the second. A similar distinction is carried out in the collections of systematic botany in the natural history branch of the BritishMuseum, with the additional advantage of close contiguity; indeed, as an example of a scheme of good museum arrangement (although not perfect yet in details) I cannot do better than refer to the upper story of the east wing of that institution. The same principles, little regarded in former times in this country, and still unknown in some of the largest Continental museums, are gradually pervading every department of the institution, which, from its natonal character, its metropolitan position, and exceptional resources, ought to illustrate in perfection the ideal of a natural history museum. In fact, it is only in a national institution that an exhaustive research collection in all branches of natural history, in which the specialist of every group can find his own subject fully illustrated, can or ought to be attempted.

As the actual comparison of specimen with specimen is the basis of zoological and botanical research, and as work done with imperfect materials is necessarily imperfect in itself, it is far the wisest policy to concentrate in a few great central institutions, the number and situation of which must be determined by the population and the resources of the country, all the collections, especially those containing specimens already alluded to as so dear to the systematic naturalist, known as author's "types," required for original investigations. It is far more advantageous to the investigator to go to such a collection and take up his temporary abode there, while his research is being carried out, with all the material required at his hand at once, than to travel from place to place and pick up piecemeal the information he requires, without opportunity of direct comparison of specimens.

I do not say that collections for special study, and even original research, should not, under particular circumstances and limitations, be formed at museums other than central national institutions, or that nothing should be retained in provincial museums but what is of a directly educational or elementary nature. A local collection, illustrating the fauna and flora of the district, should be part of every such museum; and this may be carried to almost any amount of detail, and therefore in many cases it would be very unadvisable to exhibit the whole of it. A selection of the most important objects may be shown under the conditions described above, and the remainder carefully preserved in cabinets for the study of specialists.

It is also very desirable in all museums, in order that the exhibited series should be as little disturbed as possible in arrangement, and be always available for the purpose for which it is intended, that there should be, for the use of teachers and students, a supplementary set of common objects, which, if injured, could be easily replaced. It must not be forgotten that the zealous investigator and the conscientious curator are often the direst antagonists: the one endeavours to get all the knowledge he can out of a specimen, regardless of its ultimate fate, and even if his own eyes alone have the advantage of it; the other is content if a limited portion only is seen, provided that can be seen by everyone both now and hereafter.

Such, then, is the primary principle which ought to underlie the arrangement of all museums—the distinct separation of the two objects for which collections are made; the publicly exhibited collection being never a store-room or magazine, but only such as the ordinary visitor can understand and profit by, and the collection for students being so arranged as to afford every facility for examination and research. The improvements that can be made in detail in both departments are endless, and to enter further into their consideration would lead me far beyond the limits of this address. Happily, as I said before, the subject is receiving much attention.

I would willingly dwell longer upon it—indeed I feel that I have only been able to touch slightly and superficially upon many questions of practical interest, well worthy of more detailed consideration—but time warns we that I must be bringing this discourse to a close, and I have still said nothing in reference to subjects upon which you may expect some words on this occasion. I mean those great problems concerning the laws which regulate the evolution of organic beings, problems which agitate the minds of all biologists of the present day, and the solution of which is watched with keen interest by a far wider circle—a circle, in fact, coincident with the intelligence and education of the world. Several communications connected with these problems will be brought before the sectional meetings during the next few days,

and we shall have the advantage of hearing them discussed by some of those who, by virtue of their special attention to and full knowledge of these subjects, are most competent to speak with authority. It is therefore for me rather delicate ground to tread upon, especially at the close of a discourse mainly devoted to another question. I will, however, briefly point out the nature of the problems and the lines which the endeavour to solve them will probably take, without attempting to anticipate the details which you will doubtless hear most fully and ably stated elsewhere.

I think I may safely premise that few, if any, original workers at any branch of biology appear now to entertain serious doubt about the general truth of the doctrine that all existing forms of life have been derived from other forms by a natural process of descent with modification, and it is generally acknowledged that to the records of the past history of life upon the earth we must look fo the actual confirmation of the truth of a doctrine whicr accords so strongly with all we know of the present hish tory of living beings.

Professor Huxley wrote in 1875 :—"The only perfectly safe foundation for the doctrine of evolution lies in the historical, or rather archæological, evidence that particular organisms have arisen by the gradual modification of their predecessors, which is furnished by fossil remains. That evidence is daily increasing in amount and in weight, and it is to be hoped that the comparisons of the actual pedigree of these organisms with the phenomena of their development may furnish some criterion by which the validity of phylogenic conclusions deduced from the facts of embryology alone may be satisfactorily tested."

Palæontology, however, as we all know, reveals her secrets with no open hand. How can we be reminded of this more forcibly than by the discovery announced scarcely three months ago by Professor Marsh of numerous mammalian remains from formations of the Cretaceous period, the absence of which had so long been a source of difficulty to all zoologists? What vistas does this discovery open of future possibilities, and what thorough discredit, if any were needed, does it throw on the value of negative evidence in such matters! Bearing fully in mind the necessary imperfection of the record we have to deal with, I think that no one taking an impartial survey of the recent progress of palæontological discovery can doubt that the evidence in favour of a gradual modification of living forms is still steadily increasing. Any regular progressive series of changes of structure coinciding with changes in time can of course only be expected to be preserved and to come again before our eyes under such a favourable combination of circumstances as must be of most rare occurrence; but the links, more or less perfect, of many such series are continually being revealed, and the discovery of a single intermediate form is often of immense interest as indicating the path along which the modification from one apparently distinct form to another may have taken place.

Though palæontology may be appealed to in support of the conclusion that modifications have taken place as time advanced, it can scarcely afford any help in solving the more difficult problems which still remain as to the methods by which the changes have been brought about.

Ever since the publication of what has been truly described as the "creation of modern natural history," Darwin's work on the "Origin of Species," there has been no little controversy as to how far all the modifications of living forms can be accounted for by the principle of natural selection or preservation of variations best adapted for their surrounding conditions, or whether any, and if so what, other factors have taken part in the process of organic evolution.

It certainly cannot be said that in these later times the controversy has ended. Indeed, those who are acquainted with scientific literature must know that notes struck at the last annual meeting of this Association produced a series of reverberations, the echoes of which have hardly yet died away.

Within the last few months also two important works have appeared in our country, which have placed in an accessible and popular form many of the data upon which the most prevalent views on the subject are based.

The first is "Darwinism: an Exposition of the Theory of Natural Selection, with some of its Applications," by Alfred Russel Wallace. No one could be found so competent to give such an exposition of the theory as one who was, simultaneously with Darwin, its independent originator, but who, by the title he has chosen no less than by the contents of the book, has, with rare modesty and self-abnegation, transferred to his fellow-labourer all the merit of the discovery of what he evidently looks upon as a principle of overwhelming importance in the economy of nature: "supreme," indeed, he says, "to an extent which even Darwin himself hesitated to claim for it."

The other work I refer to is the English translation of the remarkable "Essays upon Heredity and Kindred Biological Problems," by Dr. August Weismann, published at the Oxford Clarendon Press, in which is fully discussed the very important but still open question—a question which was brought into prominence at our meeting at Manchester two years ago—of the transmission or non-transmission to the offspring of characters acquired during the lifetime of the parent.

It is generally recognised that it is one of the main elements of Darwin's, as well as of every other theory of evolution, that there is in every individual organic being an innate tendency to vary from the standard of its predecessors, but that this tendency is usually kept under the sternest control by the opposite tendency to resemble them, a force to which the terms "heredity" and "atavism" are applied. The causes of this initial tendency to vary, as well as those of its limits and prevailing direction, and the circumstances which favour its occasional bursting through the constraining principle of heredity, offer an endless field for speculation. Though several theories of variation have been suggested, I think that no one would venture to say we have passed beyond the threshold of knowledge of the subject at present.

Taking for granted, however, as we all do, that this tendency to individual variation exists, then comes the question, What are the agents by which, when it has asserted itself, it is controlled or directed in such a manner as to produce the permanent or apparently permanent modifications of organic structures which we see around us? Is "survival of the fittest" or preservation by natural selection of those variations best adapted for their surrounding conditions (the essentially Darwinian or still more essentially Wallacian doctrine) the sole or even the chief of these agents? Can isolation, or the revived Lamarckian view of the direct action of the environment, or the effects of use or disuse accumulating through generations, either singly or combined, account for all? or is it necessary to invoke the aid of any of the numerous subsidiary methods of selection which have been suggested as factors in bringing about the great result?

Anyone who has closely followed these discussions, especially those bearing most directly upon what is generally regarded as the most important factor of evolution—natural selection, or "survival of the fittest,"—cannot fail to have noticed the appeal constantly made to the advantage, the utility, or otherwise of special organs or modifications of organs or structures to their possessors. Those who have convinced themselves of the universal application of the doctrince of natural selection hold that every particular structure or modification of structure must be of utility to the animal or plant in which it occurs, or to some ancestor of that animal or plant, otherwise it could not have come into existence; the only reservation being for cases which are explained by the principle which Darwin called "correlation of growth." Thus the extreme natural selectionists and the old-fashioned school of teleologists are so far in agreement.

On the other hand, it is held by some that numerous structures and modifications of structures are met with in nature which are manifestly useless; it is even confidently stated that there are many which are positively injurious to their possessor, and therefore could not possibly have resulted from the action of natural selection of favourable variations. Organs or modifications when in an incipient condition are especially quoted as bearing upon this difficulty. But here, it seems to me, we are continually appealing to a criterion by which to test our theories of which we know far too little, and this (though often relied upon as the strongest) is, in reality, the weakest point of the whole discussion.

Of the variations of the form and structure of organic bodies we are beginning to know something. Our museums, when more complete and better organised, will teach us much on this branch of the subject. They will show us the infinite and wonderful and apparently capricious modifications of form, colour, and of texture to which every most minute portion of the organisation of the innumerable creatures which people the earth is subject. They will show us examples of marvellously complicated and delicate arrangements of organs and tissues in many of what we consider as almost the lowest and most imperfectly organised groups of beings with which we are acquainted. But as to the use of all these structures and modifications in the economy of the creatures that possess them, we know, I may almost say, nothing, and our museums will never teach us these things. If time permitted I might give numerous examples in the most familiar of all animals, whose habits and actions are matters of daily observation, with whose life-history we are as well acquainted almost as we are of our own, of structures the purposes of which are still most doubtful. There are many such even in the composition of our own bodies. How, then, can we expect to answer such questions when they relate to animals known to us only by dead specimens, or by the most transient glimpses of the living in a state of nature, or when kept under the most unnatural conditions in confinement? And yet this is actually the state of our knowledge of the vast majority of the myriads of living beings which inhabit the earth. How can we, with our limited powers of observation and limited capacity of imagination, venture to pronounce an opinion as to the fitness or unfitness for its complex surroundings of some peculiar modification of structure found in some strange animal dredged up from the abysses of the ocean, or which passes its life in the dim seclusion of some tropical forest, and into the essential conditions of whose existence we have at present no possible means of putting ourselves in any sort of relation?

How true it is that, as Sir John Lubbock says, "we find in animals complex organs of sense richly supplied with nerves, but the functions of which we are as yet powerless to explain. There may be fifty other senses as different from ours as sound is from sight; and even within the boundaries of our own senses there may be endless sounds which we cannot hear, and colours as different as red from green of which we have no conception. These and a thousand other questions remain for solution. The familiar world which surrounds us may be a totally different place to other animals. To them it may be full of music which we cannot hear, of colour which we cannot see, of sensations which we cannot conceive."

The fact is that nearly all attempts to assign purposes to the varied structures of animals are the merest guesses and assumptions. The writers on natural history of the early part of the present century, who "for every why must have a wherefore," abound in these guesses, which wider knowledge shows to be untenable. Many of the arguments for or against natural selection, based upon the assumed utility or equally assumed uselessness of animal and vegetable structures, have nothing more to recommend them. In fact, to say that any part of the organisation of an animal or plant, or any habit or instinct with which it is endowed, is useless, or even injurious, seems to me an assumption which, in our present state of knowledge, we are not warranted in making. The time may come when we shall have more light, but infinite patience and infinite labour are required before we shall be in a position to speak dogmatically on these mysteries of nature—labour not only in museums, laboratories, and dissecting-rooms, but in the homes and haunts of the animals themselves, watching and noting their ways amid their natural surroundings, by which means alone we can endeavour to penetrate the secrets of their life-history. But until that time comes, though we may not be quite tempted to echo the despairing cry of the poet, "Behold, we know not anything," a frank confession of ignorance is the most straightforward, indeed the only honest position we can assume when questioned on these subjects.

However much we may be convinced of the supreme value of scientific methods of observation and of reasoning, both as mental training of the individual and in the elucidation of truth and advancement of knowledge generally, it is impossible to be blind to the fact that we, who are engaged with the investigation of those subjects which are commonly accepted as belonging to the domain of physical science, are unfortunately not always, by virtue of being so occupied, possessed of that most precious gift, "a right judgment in all things."

No one intimately acquainted with the laborious and wavering steps of scientific progress (I can answer at least for one branch of it) can look upon that progress with a perfect feeling of satisfaction.

Can it be said of any of us that our observations are always accurate, the materials on which they are based always sufficient, our reasoning always sound, our conclusions always legitimate? Is there any subject, however limited, of which our knowledge can be said to have reached finality? Or if it happens to any of us as to—

> A man who looks at glass
> On it may stay his eye,
> Or if he pleases through it pass
> And then the heavens espy,

are not those heavens which are beyond the immmediate objects of our observation coloured by our prejudies, prepossessions, emotions, or imagination, as often as they are defined by any profound insight into the depth of nature's laws? In most of these questions an open mind and a suspended judgment appear to me the true scientific position, whichever way our inclinations may lead us.

For myself, I must own that when I endeavour to look beyond the glass, and frame some idea of the plan upon which all the diversity in the organic world has been brought about, I see the strongest grounds for the belief, difficult as it sometimes is in the face of the strange, incomprehensible, apparent defects in structure, and the far stranger, weird, ruthless savagery of habit, often brought to light by the study of the ways of living creatures, that natural selection, or survival of the fittest, has, among other agencies, played a most important part in the production of the present condition of the organic world, and that it is a universally acting and beneficent force continually tending towards the perfection of the individual, of the race, and of the whole living world.

I can even go further and allow my dream still thus to run—

> Oh yet we trust that somehow good
> Will be the final goal of ill,—
>
> That nothing walks with aimless feet,
> That not one life shall be destroyed
> Or cast as rubbish to the void
> When God hath made the pile complete.

A Cause of Error in Detecting and Determining Albumen.—C. Patein.—After determining albumen by heat and acetic acid it is necessary to ascertain if the filtrate does not yield a further precipitate with nitric acid.—*Comptes Rendus*, Vol. cix., No. 7.

THE LUNDBERG CASE.†

By ELWYN WALLER, Ph.D.

(Concluded from p. 119).

Resumé of Results on Phosphorus.

Number of Analysts :—15.

Number of Determinations :—NB GPH, 65 ; SBVE, 34 ; NB^B BK, 35.

Maximum Variations of Different Analysts upon the Same Pigs :—

NB GPH, 0·0419 (A. H. Sherrerd) to 0·053 (J. M. Sherrerd). Diff. = 0·0111.

SBVE 0·0336 (T. M. Drown) to 0·044 (A. S. Bertolet). Diff. = 0·0104.

NB^B BK, 0·0405 (T. M. Drown) to 0·050 (A. S. Bertolet). Diff. = 0·0095.

Maximum Variations in the Same Brand :—

NB GPH, 0·02 [sample *a* (S. B. Sharples)] to 0·0544 [sample *f* (J. M. Sherrerd)]. Diff. = 0·0344.

SBVE, 0·033 [sample *d* (E. B. Hills)] to 0·0424 [sample *g* (J. M. Sherrerd)]. Diff. = 0·0094.

NB^B BK, 0·0402 [sample *k* (A. S. McCreath)] to 0·050 [sample *b* (A. S. Bertolet)]. Diff. = 0·0098.

Results for Sulphur.

As the case was made to turn chiefly on the percentage of phosphorus present in the iron, many of the analysts made no examination for either sulphur or silicon.

Resumé of Results on Sulphur.

Number of Analysts :—11.

Number of Determinations :—NB GPH, 12 ; SBVE, 15 ; NB^B BK, 12.

Sulphur.

Analyst.	Sample.	Grms. taken.	Method of Analysis.	Furnace Marks. NB GPH.	SBVE.	NB^B BK.
S. B. Sharples	*a*	—	A Dir.	trace	trace	trace
A. H. Elliott	*c*	5	Cl filtr.	none	none	none
E. B. Hills	*d*	—	—	none	none	none
J. M. Sherrerd	*e*	—	—	—	0·011	—
P. W. Shimer	,,	7	Ev. Mn.	—	0·019, 0·013	—
A. S. Bertolet	*f*	—	—	0·038	—	—
A. M. Sherrerd	*l*	5	Ev. Mn.	0·3005	0·0008	0·00067
T. M. Drown	,,	5—6	Ev. Mn.	0·024	0·033	0·019
S. A. Ford	,,	4—5	A Dir.	0·0085, 0·0052	0·0102, 0·0075	0·0167, 0·0166
W. O. Wuth	,,	10	Ev. Pb.	0·018	0·020	0·023
T. H. Garrett	,,	—	—	trace	0·007, 0·005	0·011, 0·007
A. S. Bertolet	,,	—	—	0·039	0·027	0·023
J. M. Sherrerd	,,	—	—	0·0074	—	0·011

In the table of results, under methods of analysis, the letters A, N, and Cl have the same significance as to the solvents used as in the phosphorus table. *Dir.* signifies that the precipitation of the barium sulphate was effected in presence of all the iron after solution. *Ev.*, that the sulphur was set free from the sample by treatment. *Filtr.*, that the iron in this solution was precipitated out by ammonia, and the sulphur determined in the filtrate with HCl in a suitable apparatus. *Mn*, that the gas thus evolved was passed through a solution of potassium permanganate (Drown, *Am. Chem. Journ.*, iv., 423). *Pb*, that it was passed through a solution of lead salt.

Methods used for the Determination of Sulphur.

The "direct" method used by Mr. Ford was described by him as having been performed thus:—The iron was dissolved in nitric acid with addition of a little hydrochloric; after effecting solution more hydrochloric acid was added, and the solution evaporated to dryness and heated, the mass taken up with hydrochloric acid, and the solution evaporated until ferric chloride began to crystallise out. It was then diluted, filtered, barium chloride solution added, and the mixture allowed to stand (warm) over night, then filtered, &c., as usual. Mr. Sharples appears to have followed essentially the same method.

Mr. Elliott precipitated the iron with ammonia in the solution filtered from the silica, and in the filtrate from the iron added barium chloride after acidulating.

The evolution method used by Messrs. Drown, Shimer, and A. H. Sherrerd is the one sometimes known as "Drown's method for sulphur." It consists in treating the iron in a flask with hydrochloric acid, and passing the gases evolved through potassium permanganate solution; after destroying the excess of permanganate by heating with hydrochloric acid the sulphur was precipitated with barium chloride. Messrs. Drown and Shimer testified to treating the residue in the evolution-flask with aqua regia to recover any sulphur that might have been retained.

Dr. Wuth used the same mode of expelling the sulphur from its combination with the iron, but previously filled the evolution-flask with hydrogen, and the evolved gases were by him passed through an alkaline solution of lead. The precipitate, consisting chiefly of lead sulphide, was fused with alkaline carbonate and nitrate, and in the solution from this fusion, after evaporation to dryness with hydrochloric acid, the barium precipitation was conducted as usual.

Maximum Variations of Different Analysts on the Same Pigs :—

NB GPH, trace (T. H. Garrett) to 0·039 (A. S. Bertolet) Diff. = 0·039.

SBVE, 0·0008 (A. M. Sherrerd) to 0·033 (T. M. Drown). Diff. = 0·0322.

NB^B BK, 0·00067 (A. M. Sherrerd) to 0·023 (W. O Wuth and A. S. Bertolet). Diff. = 0·02233.

Maximum Variations in the Same Brand :—

NB GPH, none [sample *c* (A. H. Elliott) and *d* (E. B. Hills)] to 0·039 [sample *l* (A. S. Bertolet)].

SBVE none [samples *c* (A. H. Elliott) and *d* (E. B. Hills) to 0·033 [sample *l* (T. M. Drown)].

NB^B BK none [samples *c* (A. H. Elliott) and *d* (E. B. Hills)] to 0·023 [sample *l* (Wuth and Bertolet)].

Results for Silicon.

In the table as before, under "methods of analysis," the first letters are intended to suggest the solvent used. The other abbreviations used will be explained in the fuller descriptions of the methods.

Messrs. Drown, A. M. Sherrard, and Shimer used the method known as Drown's,* which consists in beginning

† From the *School of Mines Quarterly*, Vol. x., No. 3, April, 1889.

* *Trans. Am. Inst. Min. Eng.*, vii., 346.

Silicon.

Analyst.	Sample.	Grms. taken.	Method of Analysis.	Furnace Marks. NB GPH.	SBVE.	NB^B BK.
S. B. Sharples.. ..	*a*	—	A	0·72	1·05	0·69
A. H. Elliott	*c*	5	Cl +	0·979, 0·971	1·113	1·192
E. B. Hills	*d*	—	—	0·96	0·9	0·95
J. M. Sherrerd.. ..	*e*	—	—	—	0·87	—
P. W. Shimer	,,	1	N Drown.	—	0·841, 0·822	—
A. S. Bertolet	*f*	—	—	0·813	—	—
J. M. Sherrerd.. ..	,,	—	—	0·961	—	—
A. M. Sherrerd ..	*l*	5?	N Drown.	1·106, 1·120	0·812, 0·812	1·26, 1·26
T. M. Drown	,,	1—1·5	N Drown.	1·112, 1·152	0·838, 0·832	1·237, 1·234
S. A. Ford	,,	2—3	HCl loss KHO	1·065, 1·061	0·801, 0·781	1·190, 1·190
T. H. Garrett	,,	3—4	N loss HF +	1·116, 1·107	0·822, 0·821	1·239, 1·232
A. S. Bertolet	,,	—	—	1·058	0·769	1·177
J. M. Sherrerd.. ..	,,	—	—	1·078	—	1·195
W. O. Wuth	,,	2	N HCl fus.	1·05	0·77	1·190

solution with nitric acid, then adding sulphuric in sufficient excess, and dehydrating the silica by evaporating down to concentrated sulphuric acid. Mr. Elliott ignited and weighed the residue obtained by evaporation of the solution of the portion taken for phosphorus. The + sign in the table signifies that that portion of the sample was used for some other determination. Dr. Wuth purified the residue left by evaporation of the first acid solution of the iron by fusion with alkaline carbonate, solution in hydrochloric acid, and re-evaporation. Messrs. Garrett and Ford determined the silica by loss, Mr. Garrett taking the residue left by evaporation of the portion taken for phosphorus, and, after ignition and weighing, expelling by means of hydrofluoric acid. On the other hand, Mr. Ford took a separate portion, dissolved in hydrochloric acid (Gr. 1·06), evaporated to dryness, weighed the residue, boiled it with KOH solution (Gr. 1·25), diluted with an equal bulk of water, and again filtered and weighed.

Resumé of Results on Silicon.

Number of Analysts :—11.

Number of Determinations :—NB GPH, 17; SBVE, 16; NB^B BK, 14.

Maximum Variations of Different Analysts on the Same Pigs :—

NB GPH, 0·813 (A. S. Bertolet) to 0·961 (J. M. Sherrerd). Diff. = 0·148.

SBVE, 0·769 (A. S. Bertolet) to 0·838 (T. M. Drown). Diff. = 0·069.

NB^B BK, 1·177 (A. S. Bertolet) to 1·26 (A. M. Sherrerd). Diff. = 0·083.

Maximum Variations in the Same Brand :—

NB GPH, 0·72 [sample *a* (S. P. Sharples)] to 1·152 [sample *l* (T. M. Drown)]. Diff. = 0·432.

SBVE, 0·769 [sample *l* (A. S. Bertolet)] to 1·113 [sample *c* (A. H. Elliott)]. Diff. = 0·344.

NB^B BK, 0·69 [sample *a* (S. P. Sharples)] to 1·26 [sample *l* (A. M. Sherrerd)]. Diff. = 0·570.

Conclusions.

A fair conclusion from these results would seem to be that, as regards *phosphorus*, different analysts having portions of the same pig-iron may obtain results differing from one another by about 0·01 per cent, also that in the same brand of iron about the same difference in phosphorus is to be expected.

As regards *sulphur*, when small in amount the differences to be expected between different analysts on portions of the same pig, or between different samples of the same brand, are comparatively great and very irregular, and hence we must conclude either that sulphur is very irregularly distributed through the iron, or that our present methods of determining that element in manufactured irons need careful revision. Probably both aspects of the case require attention.

As regards *silicon*, portions of the same pig in different hands may show results differing from one another by 0·1 per cent or over; in the same brand the differences may be in the neighbourhood of 0·5 per cent.

As to methods of analysis, there seems to be no good reason for giving a preference to one over any of the others used by the different analysts. In many cases results agreeing closely were obtained on the same sample by different methods, and further, where the same analyst tried the effect of different methods, his results were essentially the same.

CLARKE'S SOAP TEST: PREPARTION OF THE STANDARD SOLUTION.

By F. E. NELSON.

It has long been recognised among chemists that Clarke's soap test, as a measure of the hardness of natural waters, is of only limited application and value.

Mr. A. H. Allen, in a recent paper (*Journ. Soc. Chem. Ind.*, Dec., 1888), has critically discussed, and clearly shown, the defects of the test, at the same time substituting a method of examination of evident superiority; nevertheless, the soap test will not be banished from the laboratory, and I venture to make a suggestion of a very simple method of preparing a standard soap solution of constant composition, which will be sufficiently explained by the following example:—

One grm. of pure palmitic acid was dissolved in a small volume of pure spirit, and neutralised with 4 c.c. normal soda solution (calc. equiv., 3 9 c.c.). This volume of soda solution is equivalent to 4 × 50 m.grms. $CaCO_3$, and was therefore diluted to 200 c.c., adding so much aqueous spirit that the percentage of alcohol in the standard solution amounted to 35.

This solution I found to give constant results, which, with waters containing only calcium carbonate, are closely approximate to the contents of $CaCO_3$, as determined by titration.

Instead of a pure palmitic acid, fat acids separated from ordinary tallow may be used, neutralising in presence of phenol-phthalein, as indicator, and diluting in accordance with the number of c.c. of normal alkali used.

Laboratory of Messrs. Cross and Bevan,
4, New Court, London, W.C.,
Sept. 3, 1889.

The Presence of Living Germs in Preserved Foods.—MM. Poincarré and Macé.—The authors have detected bacteria in the following "tinned" meats:—Salt beef, ragout of hare, ox tongues, partridge, larks, sardines, salmon, and tunny, and in two vegetables, kidney beans and spinach.—*Journ. de Pharm. et de Chim.*, xix., No. 11.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 7, August 12, 1889.

The Production of Crystalline Cobaltous and Ferrous Hydrates.—A. de Schulten.—The cobaltous compound is prepared by heating a solution of 10 grms. cobaltous chloride in 60 c.c. water with 250 grms. caustic potassa in a flask of Bohemian glass into which is passed a current of coal-gas. As the temperature rises the cobaltous chloride dissolves in the potassa, which turns to a deep blue. The solution is let settle for twenty-four hours, keeping the flask full of coal-gas. Cobaltous hydrate appears to the naked eye as a deep violet powder, which, under the microscope, appears in quadrangular prismatic crystals. Ferrous hydrate is obtained in a corresponding manner, using soda instead of potassa. Nickel hydroxide is perfectly insoluble in the strongest solutions of potassa and soda.

Journal de Pharmacie et de Chimie. Series 5, Vol. xix., No. 11.

Use of Potassium Permanganate to Detect the Impurities of Alcohol. — P. Cazeneuve. — Already noticed.

Comparative Study of Products obtained by the Fermentation of Amylaceous Matters by Means of Various Kinds of Ferments.—M. Martinand.—Already noticed.

Conversion of Nitro-camphor into Nitroso-camphor.—P. Cazeneuve.—Already noticed.

Analysis of Cinchonas and the Relative Solubility of the Proximate Principles which they Contain in Water, Alcohol, and Dilute Hydrochloric Acid.—E. Landrin.—Already noticed.

Toxicological Search for Mercuric Chloride.—Prof. Ludwig.—The suspected organs are first boiled for several hours with nitric acid. When the mass is completely reduced to a pulp it is placed in a flask (connected to a refrigerator) filled with hydrochloric acid of mean concentration and heated for three or four hours, taking care to stir well. It is then let cool slightly and the liquid is decomposed by means of a small quantity of potassium chlorate; the mixture is filtered to separate the insoluble precipitate and zinc-powder is added. It is stirred for a minute, let settle, and heated again to 50° or 60°, taking care to stir well in order to obtain a complete settlement of the mercury. After letting settle for a day, a small quantity of zinc-powder is again added and the whole process is repeated. The solution is decanted afresh, the collected precipitates are filtered through a funnel stoppered with asbestos, washed, and dried in a current of air. To separate the mercury from the zinc amalgam the author makes use of a tube bent in U-shape at one end, into which there is introduced first a little asbestos, then a layer of lime, then a layer of copper-oxide, and finally the zinc-amalgam. The curved part of the tube which issues out of the furnace is kept cool by means of water. The lime is first heated to redness, then the copper, and lastly the amalgam. A current of air is continually passed through the tube. The mercury separates in drops in the refrigerated part of the apparatus. In this manner, from 97·5 to 98 per cent of the mercury is recovered. Mercury is localised in certain special organs, especially the liver, the spleen, and the kidneys.

Part Played by Alum in Bread-making. — M. Bruylants (see *Journal de Pharmacie*, vol. xix., p. 421).—Alum owes its power of blanching the paste of bread no to the alumina which it contains or to the combination o this earth with the gluten, but to the sulphuric acid liberated by the formation of aluminium albuminate. According to Nothnagel and Rossbach the prolonged daily use of alum in the proportion of 0·05 to 0·1 grm. occasions gastric disturbances not unimportant. The author finds that the artificial gastric digestion of alumed bread effects the solution of all the alum present. Hence it is possible that a quantity of alumina equivalent to 0·20 grm. of alum may enter the circulation daily.

Journal fur Praktische Chemie. Vol. xxxix., Nos. 10 and 11, 1889.

On Pentamethylene and Tetramethylene Bromides.—G. Gustavson and N. Demjanoff.—The boiling-point of pentamethylene is between 204° and 206°, much higher than the boiling-points of all the known amylene bromides. The boiling-point of tetramethylene is between 188° and 190°.

Remarks on a Memoir by Hanriot and Bouveault.—E. von Meyer.—The author shows that he had ascertained the composition and the constitution of the compounds $C_6H_9NaN_2$ and $C_6H_{10}N_2$ four months prior to MM. Hanriot and Bouveault.

MISCELLANEOUS.

Determination of Copper and Arsenic in Pyrites.—R. Nahnsen (*Chemiker Zeitung*).—For determination of copper 12·5 grms. of the dry finely pulverised sample are placed in a beaker of thin glass 17 centimetres in height, and covered with 10 c.c. water and 1 c.c. strong sulphuric acid. Keeping the glass covered with a porcelain capsule, nitric acid of sp. gr. 1·4 is gradually added until effervescence no longer occurs. The liquid is let boil over a moderately strong flame, the porcelain capsule is removed, and the liquid is boiled, whilst being frequently shaken round and round until it becomes tough and scarcely yields to shaking, and yellow saline particles begin to separate out. The paste is then quickly brought into solution by means of warm water, which should be kept ready at hand. The cold solution is transferred to a 250 c.c. flask, filled up, and filtered through a dry filter. 200 c.c. (=10 grms. pyrites) of the solution thus freed from silica and lead are treated for some hours with a brisk current of sulphuretted hydrogen until the precipitate clots together and the liquid appears transparent. It is filtered and washed with pure water, whilst being frequently crushed with a glass rod. Sulphuretted hydrogen water is here unnecessary if the sulphuretted hydrogen has been allowed to act until the liquid appears quite clear. The portion of the precipitate on the filter is rinsed back with a minimum of hot water to the main mass, and so much strong solution of sodium sulphide is added that the liquid, after being heated to a boil for a few minutes, shows no undissolved sulphur. It is diluted with hot water, let stand in a warm place until clear; the solution which contains the arsenic and antimony, and is quite free from copper, is filtered off, and the deposit of copper sulpide is washed with hot water. Traces of iron sulphide which still adhere to the copper sulphide are removed by hot water to which a few drops of hydrochloric acid have been added, the residue is washed until free from chlorine, and the copper determined as sulphide. The copper sulphide is tested for the presence of cadmium or bismuth by dissolving it in nitric acid and treating the solution for some time with ammonium carbonate in heat. The precipitate formed is weighed as oxide and deducted. For determining the arsenic the dissolved sulphuretted hydrogen is expelled from the 200 c.c. of solution by a current of carbonic acid, and arsenic sulphide is extracted from the washed precipitate by means of ammonia. The further treatment may be conducted volumetrically (Leroy W. McCay, Chemical News, xlviii., 7) or gravimetrically (B. Fischer, *Chemiker Zeitung*, ix., 1613).

The Chemical Laboratory of Wiesbaden always enjoys a very large attendance. For the summer term, 1889, there were 68 students on the books; 54 of these worked only in the chemical laboratory, 10 in the bacteriological department, and 4 in both departments. 44 were from Germany, 6 from England, Ireland, and Scotland, 4 from North America, 3 from Holland, 3 from Russia, 2 from Italy, 1 from Luxemburgh, 1 from France, 1 from Spain, 1 from Norway, 1 from Chili, and 1 from Australia. The assistants in the instruction laboratory are 2 in number, in the private laboratory 15, and in the versuchsstation 3. At the end of the summer term, 1889, Dr. med. F. Hueppe left the laboratory because he has been appointed Professor of hygiene at the German University in Prague. His successor is Dr. med. G. Frank, late assistant of Professor von Pettenkofer in Munich, and of Professor Rob. Koch in Berlin. The other teachers are the same as hitherto. The winter term begins on the 15th of October. Besides the scientific researches, a great number of analyses were undertaken in the different departments of the laboratory and the versuchsstation on behalf of manufacture, trade, mining, agriculture, and hygiene.

NOTES AND QUERIES.

Brewing.—Can any of your readers recommend me a good and not too voluminous work upon the chemistry of brewing?—K.

Tests for Alum.—Could any of your readers give me a few simple tests for alum, either soda or potash? I have been unable to find tests given in any works on the subject.—A TYRO.

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Formerly Professor of Chemistry in the University of Heidelberg.

Translated by GEORGE M'GOWAN, Ph.D.,

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CHEMISTRY COURSE.

Full particulars of this Course, qualifying for the Victoria University DEGREES in CHEMISTRY and the COLLEGE TECHNOLOGICAL CHEMISTRY CERTIFICATE, will be forwarded on application. The Session commences October 1st.

H. W. HOLDER, M.A., Registrar.

NEW SOUTH WALES.

THE GOVERNMENT OF NEW SOUTH WALES intend to establish METALLURGICAL WORKS on a scale sufficiently large for determining, in bulk, the best methods of treating Ores produced in the Colony.

A SUPERINTENDENT is REQUIRED to erect, control, and direct these Works. He must possess the highest qualifications and widest experience, and it will be his duty to introduce the best methods of treating Ores (especially Auriferous and Argentiferous), with a view to extract therefrom the metals and other substances possessing an economic value. He would also have to impart full instruction in the various methods of treatment, and to afford every facility to Smelters and Miners for acquiring a practical knowledge of the processes employed.

Applications, stating Candidate's age, salary required, and accompanied by copies of testimonials, must be sent, on or before the 25th September, 1889, to The Agent-General for New South Wales, 5, Westminster Chambers, London, S.W.

SAUL SAMUEL,

7th August, 1889. Agent-General for New South Wales.

CHEMICAL LABORATORY,
WIESBADEN, GERMANY.

Director—Prof. R. FRESENIUS, Ph.D.

Practical Instruction in the Laboratory .. .. Prof. R. FRESENIUS, Ph.D. / Prof. H. FRESENIUS, Ph.D. / W. FRESENIUS, Ph.D. / E. HINTZ, Ph.D.

LECTURES.

Experimental Chemistry (Inorganic) — Prof. H. FRESENIUS, Ph.D.
Experimental Physics .. .. / Stöchiometry .. .. — W. FRESENIUS, Ph.D.
Organic Chemistry .. .. — E. HINTZ, Ph.D.
Chemical Technology .. .. / Microscopy, with exercises in Microscopic work .. .. — E. BORGMANN, Ph.D.
Chemistry and Analysis of Foods .. — Prof. H. FRESENIUS, Ph.D. / E. BORGMANN, Ph.D. / W. FRESENIUS, Ph.D., and E. HINTZ, Ph.D.
Hygiene .. .. / Practical exercises in Bacteriology .. — Dr. med. G. FRANK.
Technical Drawing, with exercises .. — J. BRAHM.

The next Session commences on the 15th of October. The Regulations of the Laboratory and the Syllabus of Lectures will be forwarded gratis on application to C. W. KREIDEL'S Verlag, at Wiesbaden, or to the undersigned.

Prof. R. FRESENIUS, Ph.D.

THE LONDON HOSPITAL MEDICAL COLLEGE.

The WINTER SESSION will COMMENCE on TUESDAY, October 1st.

The Hospital, which is the largest general Hospital in the kingdom, contains nearly 800 beds, all in constant use. There are wards for accidents, surgical and medical cases, diseases of women and children, and ophthalmic cases. Special departments for diseases of the eye, ear, throat, skin, and teeth, and for cancer, tumours, diseases of the bladder, piles and fistula. Number of in-patients last year, 8873; out-patients, 101,548; accidents, 7456.

Surgical operations daily.

Appointments:—Resident accoucheur, house physicians, house surgeons. Forty of these appointments are made annually. Numerous dressers, clinical clerks, post-mortem clerks, and maternity assistants are appointed every three months. All appointments are free. Holders of resident appointments are also provided free board. The New College Buildings are now complete, and afford more than double the former accomodation.

Two Entrance Science Scholarships, value £60 and £40, and two Buxton Scholarships, value £30 and £20, will be offered for competition at the end of September to new Students. Sixteen other Scholarships and Prizes are given annually.

Luncheons or dinners at moderate charges can be obtained in the Students' Club.

The London Hospital is now in direct communication with all parts of the Metropolis. The Metropolitan, District, and other Railways have stations within a minute's walk of the Hospital and College.

For further information apply personally, or by letter, to

Mile End, E. MUNRO SCOTT, Warden.

Prof. A. E. FOOTE,

of Philadelphia, Pa.,

Who has the

LARGEST STOCK OF MINERALS AND CHEMICAL AND OTHER SCIENTIFIC BOOKS IN THE WORLD,

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Prof. FOOTE has brought to Paris twelve tons of choice crystallised Minerals, including such beautiful minerals as Red and Yellow Wulfenites, Red, Yellow, and Brown Vanadinites, Colemanite, Azurite, &c. Also such rare species as Colemanite, Gadolinite, Hanksite, Beryllionite, Thenardite, Trona, Borax, &c., &c.

Prof. FOOTE will be glad to meet his English customers at No. 14, RUE DESAIX, or to fill orders by express.

THE CHEMICAL NEWS.

Vol. LX. No. 1556.

HINTS TO STUDENTS.

We have in former years repeatedly endeavoured to throw some light upon the important questions, What and in what manner young men should study? To-day we are driven to consider the still more fundamental subjects, Under what circumstances they should study, and even if they should study chemistry at all? Such doubts may, perhaps, seem strangely heretical in face of the general outcry for higher instruction as a cure for the difficulty of earning a livelihood experienced by so many. But they will be found, we submit, more than justified by the present position of affairs both in Britain and elsewhere. Time was, if we may believe an ancient proverb, when "learning was better than house or land." Cultivated intelligence was rare, and, except spoiled by co-existence with dishonesty or idleness, it could almost name its own terms. But in our days the supply has outrun the demand. According to a recent investigation made at Gœttingen the number of young men studying in the different faculties of the German Universities outnumber more than two-fold the possible number of openings when their careers are completed. With us it is no better. We have heard authentic cases of University graduates and even fully qualified physicians and barristers seeking employment as railway-porters. The old learned professions, divinity, law, and medicine, being thus overcrowded, how is it with the no less learned professions of more recent date? The consulting chemist and the engineer, whether he belong to the civil, mechanical, mining, or electrical department—in the last probably less than in the others—are fast reaching, if they have not already reached, the same unenviable position. We see legally qualified medical men announcing that they give advice and medicine for sixpence, and the sums for which scientific chemists undertake to analyse all manner of substances, natural or artificial, can certainly not pay for pure reagents, leaving time out of the question. A correspondent of the Chemical News, "M.A., F.C.S., and F.I.C.," tells us what he was offered for some analytical work. The parties required about 36 samples weekly to be analysed for total solids and butter-fat during the whole season from April to November. For this entire work the parties concerned had previously paid £20, or something less than 4d. per sample! This unpleasant fact stands by no means singly, and we hence submit that any young man will do well to reflect maturely before he spends considerable sums of money and some of the most important years of his life in qualifying himself for the profession of an analytical and consulting chemist.

Now we are often told, and that not without a certain share of truth, that it is merely mediocrity which is crowded, there being "always room enough at the top." The difficulty is, however, that the process of sorting out men of ability from the mass is often very tedious, and, where honours and positions are awarded on the examination system, altogether fallacious.

It must not, however, be supposed that we are seeking to dissuade the young from the study of chemistry altogether. To three classes, who we would fain hope are becoming more numerous, we must recommend it most strongly. In the first place, to all who aim at reaching something higher than a mere Board-school grade of mental culture we should recommend it, quite irrespective of possible material benefits, as a means of intellectual training. Chemistry teaches us the important arts of close and accurate observation, and of drawing correct inferences from the facts recognised. These important arts can never be mastered by the most prolonged study of classics and mathematics. Hence, if we regard education as intellectual discipline, rather than the mere absorption of a number of facts, we shall find some one of the branches of natural and physical science absolutely essential and indispensable. And under most circumstances chemistry will prove the most appropriate subject.

Another class which we should like to see largely recruited consists of men in independent circumstances who have the leisure needed for taking in hand those many scientific problems which are often neglected because they are not immediately remunerative. Such men too commonly waste their time in dissipation, in the pursuit of more wealth, or in making mischief. Now if they possess the needful ability we had much rather see them at work in the laboratory.

The last class to whom we would especially recommend a thorough study of chemical principles are those who are looking forward to employment in the chemical arts, whether as proprietors, managers, foremen, &c. It is a misfortune when men who occupy such positions depend merely upon rule of thumb and traditional recipes.

If these three classes do what we believe is their duty our national manufactures and our national habits of thought will alike undergo a needed improvement.

UNIVERSITIES AND COLLEGES.

UNIVERSITY OF LONDON.

Candidates for any Degree granted by this University are required to have passed the Matriculation Examination, and all candidates for Matriculation will henceforth be required to comply with the following instructions:—(1) Not less than five weeks before the commencement of the Examination every candidate must apply to the Registrar, by letter, for a Form of Entry, which, together with all particulars respecting the arrangements for the Examination, will be sent to him immediately on receipt of the application. (2). This form, duly filled up, must be returned to the Registrar not less than four weeks before the commencement of the Examination, and with it, in the same cover, must be sent (*a*) the candidate's certificate of age, and (*b*) his fee for the Examination. No candidate's name will be placed on the list of candidates unless his form of entry, certificate of age, and fee shall have been received at the University on or before the fourth Monday before the commencement of the Examination. As soon as possible after the closing of the list, and not previously, each candidate's certificate and fee will be acknowledged, his certificate will be returned, and a Number, by which he is to be designated throughout the Examination, will be assigned to him.

The Fee for this examination is £2.

There are two Examinations for Matriculation in each year; one commencing on the second Monday in January, and the other on the second Monday in June. The

Examination is conducted by means of Printed Papers; but the Examiners are not precluded from putting, for the purpose of ascertaining the competence of the candidates to pass, *viva voce* questions to any candidate in the subjects in which they are appointed to examine.

Candidates are not approved by the Examiners unless they have shown a competent knowledge in each of the following subjects:—Latin. Any one of the following Languages :—Greek, French, German, Sanskrit, or Arabic. The English Language, English History, with the Geography relating thereto. Mathematics. Mechanics. One of the following branches of Experimental Science:—Chemistry, Heat and Light, Magnetism and Electricity, Botany.

The Examination in Chemistry is—Chemistry of the Non-metallic Elements; including their compounds—their chief physical and chemical characters—their preparation—and their characteristic tests.

A Pass Certificate, signed by the Registrar, will be delivered to each candidate after the Report of the Examiners has been approved by the Senate.

If in the opinion of the Examiners any candidates in the Honours Division of not more than twenty years of age at the commencement of the Examination possess sufficient merit, the first six among such candidates will receive an Exhibition of thirty pounds per annum for the next two years; the second among such candidates will receive an Exhibition of twenty pounds per annum for the next two years; and the third will receive an Exhibition of fifteen pounds per annum for the next two years; such exhibitions are payable in quarterly instalments, provided that on receiving each instalment the Exhibitioner declares his intention of presenting himself either at the two Examinations for B.A., or at the two Examinations for B.Sc., or at the Intermediate Examination in Laws, or at the Preliminary Scientific M.B. Examination, and Intermediate Examination in Medicine, within three academical years from the time of his passing the Matriculation Examination.

Under the same circumstances, the fourth among such Candidates will receive a prize to the value of ten pounds in books, philosophical instruments, or money; and the fifth and sixth will each receive a prize to the value of five pounds in books, philosophical instruments, or money.

Any candidate who may obtain a place in the Honours Division at the Matriculation Examination in January is admissible to the Intermediate Examination either in Arts or in Science in the following July.

Intermediate Examination in Science.

The Intermediate Examination in Science will be held in July, 1890.

No candidate (with the exception of such as have obtained Honours at the Matriculation Examination in the preceding January) is admitted to this Examination within one academical year of the time of his passing the Matriculation Examination.

The Fee for this Examination is £5.

Examination for Honours.

Candidates for Honours in Chemistry will be examined in Inorganic Chemistry, treated more fully than in the Pass Examination. In addition, they will be examined practically in Simple Qualitative Analysis. This Examination will consist of six hours' examination by two printed papers and of six hours' practical work.

In the Examination for Honours, the Candidate, not being more than 22 years of age at the commencement of the Pass Examination, who most distinguishes himself will receive an Exhibition of £40 per annum for the next two years.

B.Sc. Examination.

The B.Sc. Examination will be held in October.

Candidates for this Examination are required to have passed the Intermediate Examination in Science at least one academical year previously.

The Fee for this Examination is £5.

Examination for Honours.

The examination for Honours in Chemistry will take place on Monday and Tuesday in the week following the Examination for Honours in Mathematics; on Monday by printed papers (chiefly on Organic Chemistry), and on Tuesday by practical examination in Qualitative and Quantitative Analysis.

The candidate, being not more than 23 years of age, who most distinguishes himself in Chemistry, will receive £50 per annum for the next two years, with the style of University Scholar.

Doctor of Science.

The examination for the Degree of Doctor of Science takes place annually within the first twenty-one days of June.

No candidate is admitted to the examination for the Degree of D.Sc. until after the expiration of two Academical Years from the time of his obtaining the Degree of B.Sc. in this University.

The Fee for this Examination is £10.

Preliminary Scientific (M.B.) Examination.*

This Examination takes place twice in each year,—once, for Pass and Honours, commencing on the third Monday in July; and once for Pass Candidates only, commencing on the third Monday in January.

No candidate shall be admitted to this Examination unless he shall have passed the Matriculation Examination, nor unless he have given notice of his intention to the Registrar at least one calendar month before the commencement of the examination.

The Fee for this examination is Five Pounds.

Examination in Subjects relating to Public Health.

A Special Examination will be held in December in subjects relating to public health.

No candidate is admitted to this Examination unless he has passed the Second Examination for the Degree of Bachelor of Medicine in this University at least one year previously; nor unless he shall have given notice of his intention to the Registrar at least two calendar months before the commencement of the Examination.

The Fee for this Examination is £5.

UNIVERSITY OF OXFORD.

Waynflete Professor of Chemistry.—W. Odling, M.A., F.R.S.

Every Student must reside in one or other of the Colleges or Halls, or in licensed lodgings, for a period of three years, passing at least two examinations in Arts, and one in either Mathematics, Natural Science, Law, Modern History, or Theology, when, if he obtain a first, second, or third class, he can take his B.A. Degree; if he do not gain such honour he has to pass a third examination in *Literis Humanioribus*.

The fee for students working in the Laboratory for three days in the week during the Term is £3; for students working every day, £5.

Scholarships of about the value of £75 are obtainable at Christ Church, Magdalen, and other colleges, by competitive examination in Natural Science.

More detailed information may be obtained from the University Calendar; from the professors; and from the Sub-Librarian in the Radcliffe Library or the Museum.

UNIVERSITY OF CAMBRIDGE.

Professor of Chemistry.—G. D. Liveing, M.A., F.R.S.

Jacksonian Professor of Natural and Experimental Philosophy.—J. Dewar, M.A., F.R.S.

The Student must enter at one of the Colleges, or as a Non-collegiate Student, and keep terms for three years by residence in the University. He must pass the previous

* Candidates who pass in all the subjects of the Preliminary Scientific (M.B.) Examination, and also pass *at the same time* in the Pure and Mixed Mathematics of the Intermediate Examination in Science, or who have previously passed the Intermediate Examination in Arts, are admissible to the B.Sc. Examination.

examination in Classics and Mathematics, which may be done in the first or second term of residence, or, through the Oxford and Cambridge Schools Examination Board, or through the Senior Local Examinations, before commencing residence. He may then proceed to take a Degree in Arts, either continuing mathematical and classical study, and passing the ordinary examinations for B.A., or going out in one of the Honour Triposes.

The scholarships, ranging in value from £20 to £80 a year, are chiefly given for mathematical and classical proficiency. Scholarships are given for Natural Science in Trinity, St. John's, St. Peter's, Clare, Christ's, Sidney, Pembroke, Caius, and Downing Colleges; the examinations being in December, at Easter, and in June and October.

The Chemical Laboratory of the University is open daily for the use of the Students. The Demonstrators attend daily to give instructions. A list of the lectures is published annually, in June, in a special number of the *Cambridge University Reporter*, which may be had from the Cambridge Warehouse, in Paternoster Row, or through any bookseller.

Non-collegiate Students are allowed to attend certain of the College Lectures and all the Professors' Lectures, and have the same University status and privileges as the other Students. Full particulars may be obtained by forwarding a stamped directed envelope to the Assistant Registrar, Cambridge, or from the *Cambridge University Calendar*.

UNIVERSITY OF DUBLIN.

TRINITY COLLEGE.

Professor of Chemistry.—J. Emerson Reynolds, M.D. F.R.S., V.P.C.S.

Assistant Lecturer.—Augustus E. Dixon, M.D., F.C.S.

Demonstrators.— William Early, F.I.C., and Emil A. Werner, F.C.S.

The general Laboratories include working accommodation for 120 Students, and the Quantitative and Research Laboratories for about 40 Students. The new Lecture Hall provides full accommodation for 300 Students. Lectures will commence about November 1st.

The Laboratories and the Lectures of the Professor of Chemistry can now be attended by Students who do not desire to reside in the University or proceed to its Degrees.

The full Course of General and Analytical Chemistry occupies three years, but a Student is free in his third year to devote most of his time to a special department of Pure or Technical Chemistry. Students can enter for any portion of the Course. The following Lectures are delivered:—

1. *Inorganic Chemistry and Chemical Philosophy*. — Elementary, first year; advanced, second year.
2. *Organic Chemistry*. — General, second year; advanced, third year.
3. *Metallurgy*.—A Course for Engineering and Technical Students.

The Laboratories are open every day from 10 to 5 o'clock (except Saturdays, when they close at 1 o'clock).

The Summer Course of Practical Chemistry for Medical Students begins during the first week in April and terminates with the first week in July.

KING'S COLLEGE.

(DEPARTMENT OF ENGINEERING AND APPLIED SCIENCE).

Professor of Chemistry.—J. M. Thomson, F.C.S.

Demonstrator of Practical Chemistry.—G. S. Johnson, F.C.S.

Assistant Demonstrator.—Herbert Jackson, F.C.S.

On Tuesday and Thursday at 10.20 a.m. Students of the First Year are admitted to the Course of Theoretical and Applied Chemistry. The Course commences with a View of the Forces which concur to the production of Chemical Phenomena, after which the laws of Chemical Attraction are discussed, and the Non-metallic elements and their principal Compounds are described.

The Metals and their principal compounds are next examined, care being taken to point out the applications of the Science to the Arts; and the processes of the different Manufactures and of Domestic Economy are explained and illustrated.

Examinations of the Class, both *vivâ voce* and by written papers, are held at intervals during the course at the usual Lecture hour.

Second Year.—Students attend in the Laboratory twice a week, on Tuesday and Friday, at 10.20, and they go through a course of Manipulation in the most important operations of Chemistry, including the first steps of Analysis.

Any Student of this Department may be admitted to this Class at any period of his study on payment of an extra fee.

Experimental and Analytical Chemistry in the Laboratory.—The object of this Class is to afford to Students who are desirous of acquiring a knowledge of analysis, or of prosecuting original research, an opportunity of doing so under the superintendence of the Professor and Demonstrator; Students may enter, upon payment of extra Fees, at any time except during the vacation, and for a period of one, three, six, or nine months, as may best suit their convenience. The laboratory hours are from ten till four daily, except Saturday, on which day the hours are from ten till one.

In addition to the Laboratory Fee, each Student defrays the expenses of his own Experiments. The amount of this expense, which is comparatively trifling, is entirely under his own control.

Special hours and fees are arranged for the convenience of such Third Year Students as wish to study Analytical Chemistry.

Fees.—Chemistry per term, £3 3s. od.; per ann., £8 8s. od.; Practical Chemistry per term, £4 4s. od.; per ann., £10 10s. od.; Experimental and Analytical Chemistry —One Month (daily attendance), £4 4s. od.; Three Months (daily attendance), £10 10s. od.; Six Months (daily attendance), £18 18s. od.; Nine Months (daily attendance), £26 5s. od. A student taking a month's ticket may attend daily during 1 month, or 3 days a week during 2 months, or 2 days a week during 3 months.

Rules as to Admission of Students.

I. The Academical Year consists of Three terms: Michaelmas Term, from beginning of October to the week before Christmas; Lent Term, from the middle of January to the week before Easter; Easter Term, from Easter to the beginning of July.

II. The days fixed for the Admission of New Students in the Academical Year 1889-90, are Tuesday, October 1, Wednesday, January 15, and Wednesday, April 16.

METALLURGY.

Professor.—A. K. Huntington, F.I.C., F.C.S., &c.

The following subjects are treated of in the Lectures: The Selection and Economic Preparation of Fuel and of Refractory Materials; the methods by which metals are obtained from their ores, and the means by which they are rendered suitable for the various requirements of the Arts.

Particular attention is made to the study of the Nature and Properties of Metals and Alloys available for Constructive Purposes.

In the Metallurgical Laboratory, which is always open during College hours, the relation between the Chemical Composition of Metals and their Mechanical Properties may be studied by the aid of Testing Machinery. The instruction given to each student is regulated by his special requirements.

PHOTOGRAPHY.

Lecturer.—J. M. Thomson, F.R.S.E., F.C.S.

Arrangements are made for a complete Course of Instruction in Photography to the students of the third year. A glass house has been erected, and in connection with it a Laboratory for the preparation of Photographic Chemicals. Students entering to this department will be

afforded every facility for practising the Art in all its branches.

In addition to the regular College Course in Photography occasional classes are formed, consisting each of about six gentlemen, who meet twice a week. The fee for private instruction is £5 5s. for ten lessons, or £10 10s. for three courses. There is in every case a charge of £1 each course for chemicals.

Evening Classes.

Classes for Evening Instruction in various subjects are held during the months from October to March, inclusive, and during the months of April, May, and June.

UNIVERSITY COLLEGE.

Faculty of Science.

Professor.—William Ramsay, Ph.D., F.R.S.

Assistant Professor.—R. T. Plimpton, Ph.D.

Assistants.—N. Collie, Ph.D., and H. Smith.

The Session is divided into three Terms, as follows, all the dates being inclusive :—

First Term, from Thursday, October 2nd, until Wednesday, December 18th;

Second Term, from Tuesday, January 7th, 1890, till Tuesday, March 25th;

Third Term, for Lectures, from Tuesday, April 15th, till Tuesday, July 1st. Class Examinations occupy about ten days, beginning on Thursday, June 19th.

Students, who having entered in October do not intend to present themselves in all three subjects at the July Preliminary Science Examination, should during the first term confine their attention to Chemistry, and take this subject alone at the January Examination.

Students entering in January should take Physics and Biology at the July Examination, and Chemistry at the succeeding January Examination.

Junior or Matriculation Course.

Tuesday, Thursday, and Saturday, at 10, commencing October 3, 1889, and April 17th, 1890. Fee :—£4 4s.

These Courses will each consist of about thirty lessons, partly theoretical and partly practical, on the non-metallic elements. Frequent exercises will be given.

Senior Course of Chemistry.

First and Second Terms : Inorganic.—The Class meets four times a week: Mondays, Wednesdays, Fridays, and Saturdays, at 9, for Lectures, Examinations, and Exercises.

Fee :—For the Course, £7 7s.; Perpetual, £9 9s.; for the First or Second Terms, £4 4s.

This Course and the Practical Class cover the subject as prescribed for the Preliminary Scientific (M.B.) and Intermediate Examination in Science of the University of London.

For the Preliminary Scientific Examination Students who take the three subjects for that examination in July attend during the First and Second Terms.

Advanced Course of Chemistry.

Second and Third Terms.—The class meets twice a week, on Tuesdays and Thursdays, at 9. The hour will be altered by special arrangement with the class if necessary.

Fee :—For the Course, £3 3s.; for a Term, £2 2s.

This Course will be found suitable for those about to proceed to graduation as Bachelor of Science in London University, and to those who intend to choose Chemistry as a profession. Such students should also work in the Laboratory during as many hours as they can spare.

Organic Chemistry.

Tuesday and Thursday, at 9, in the First Term; Tuesday, Thursday, and Saturday, at 10, in the Second Term; and Monday, Wednesday, and Friday, at 9, in the Third Term. The hour of meeting will be altered should the class desire it.

This Course of Organic Chemistry is intended for those who in studying the subject have not a Medical Examination chiefly in view. Candidates for Honours at the Int.M.B. are, however, recommended to attend this Course during the Second and Third Terms, instead of the Special Summer Course.

The Course includes the subjects required at the B.Sc. Examination, Pass and Honours; but no previous acquaintance with Organic Chemistry will be expected of those joining the Class.

Fee :—For the Course, £6 6s.; for a Term, £2 12s. 6d.

An Advanced Course for those engaged in prosecuting research in Organic Chemistry will be held three times a week during the Second Term. Fee, £2 12s. 6d.

Practical Class.

First and Second Terms, Tuesday and Thursday, at 11.

Fee, including cost of materials, £5 5s.; for a Second Course, £3 3s.

The Course includes the Practical Chemistry required at the Preliminary Scientific and Intermediate Science Examinations.

Senior Practical Class.

Fridays from 2 to 4 and Saturdays from 10 to 12 during the Third Term.

Fee :—(Including cost of materials) £5 5s.; for a Second Course, £3 3s.

Analytical and Practical Chemistry.

The Laboratory is open daily from 9 a.m. to 4 p.m., Saturdays excepted, from October until the middle of July, with a short recess at Christmas and at Easter.

Fees: for the Session, £26 5s.; six months, £18 18s.; three months, £10 10s.; one month, £4 4s.

Three specified days a week :—for the Session, £15 15s.; six months, £11 11s.; three months, £6 6s.; one month, £2 12s. 6d., exclusive of expense of materials. Students may enter at any period of the Session.

The Laboratory Course includes the Practical Chemistry required at the following Examinations of the University of London :—Prel. Sci. (M.B.), Intermediate M.B., Intermediate Science, B.Sc.

Students who wish to attend the Laboratory and Classes of Technical Chemistry may acquire here the requisite preliminary knowledge of Practical Chemistry and Analysis.

When accompanied by, or preceded by, attendance on the Lectures on Inorganic and Organic Chemistry, the Laboratory Course qualifies Students in the application of Chemistry to Manufactures, Metallurgy, Medicine, or Agriculture, &c.

There is also a Chemical Library containing the chief Journals and Standard Works on Chemistry.

A Gold Medal and Certificates of Honour are competed for by first year's Students. The Tuffnell Scholarship (£100 for two years) will also be competed for in the Session 1889-90; also the Clothworker's Scholarship of £50.

Applied Chemistry.

Lecturer, Watson Smith, F.I.C., F.C.S.

During the first and second terms Courses of Lectures will be given on the following subjects :—

Chemistry of the Alkali Trade. Tuesday, 5 to 6 p.m. Fee, £2 2s.

Fuel and Gas. Monday, 5 to 6 p.m. Fee, £2 2s.

Coal-tar Products. Thursday and Friday, 5 to 6 p.m. Fee, £3 3s.

Evening Lectures will be given by gentlemen qualified by practical and theoretical acquaintance with special subjects, and occasional visits to Works will be arranged.

Residence for Students.

Students can obtain residence at University Hall, Gordon Square. Particulars can be obtained at the office of the College.

NORMAL SCHOOL OF SCIENCE AND ROYAL SCHOOL OF MINES.

Professor.—T. E. Thorpe, Ph.D., B.Sc., F.R.S.

Assistant Professor.—F. R. Japp, M.A., Ph.D., F.R.S.

Demonstrators.—H. Chapman Jones and A. E. Tutton.

Assistants.—G. S. Newth, F. Guthrie, and J. W. Rodger.

The Normal School of Science at South Kensington is intended, primarily, for the instruction of teachers, and of students of the industrial classes selected by competition in the examinations of the Science and Art Department. The Royal School of Mines is affiliated to the Normal School. Students entering for the Associateship of the School of Mines obtain their general scientific training in the Normal School. The instruction in the Normal School is arranged in such a manner as to give the Students a thorough training in the general principles of Science, followed by advanced instruction in one or more special branches of Science. The Associateship is granted in certain divisions or lines of study. Students who go through any one of the prescribed courses of instruction and pass the necessary Examinations receive a Certificate of Associateship of the Normal School, or of the Royal School of Mines. But students who are not candidates for the Associateship are permitted to take up the course of instruction in one or more special branches of science, and on passing the examination receive a Certificate to that effect. The Associateship of the Normal School of Science is given in one or more of the following divisions:—Mechanics, Physics, Chemistry, Biology, Geology, and Agriculture, and the Associateship of the Royal School of Mines in Metallurgy and Mining.

The course of instruction, which lasts for three years, is the same for all the divisions during the first year, after which it is specialised in accordance with the Scheme detailed in the Prospectus of the School.

The Session is divided into two Terms. The first Term begins about the 4th of October and ends about the middle of February. The second Term begins in the middle of February and ends about the middle of June.

Examinations are held at the end of each course of instruction and at such other periods as may be found necessary. On the results of these examinations the successful candidates are arranged in two classes, first and second. There are also "Honours" examinations for the subjects of the third year, the successful candidate being placed in order of merit. A student obtains the Associateship who passes in all the subjects of the first two years and of the special division he selects for his Associateship. A student who goes through the prescribed course of instruction in any subject and passes the final examination in it receives a certificate to that effect.

Students who do not wish to attend the lectures are admitted for short periods to the laboratories, at the discretion of the Professors. The fees for the laboratories are £4 per month.

Students not entering for the Associateship are admitted to any particular course of study, so far as there is room, on payment of the fees shown in the following table:—

	Lectures.	Laboratory.
	£	£
Chemistry	3	13
Physics	5	12
Biology with Botany	5	12
Geology with Mineralogy ..	4	8
Mechanics	4	6
Metallurgy	2	13
Mining	4	
Agriculture	4	10
Astronomical Physics	2	

Mathematics and Mechanical Drawing £3 per term. Geometrical Drawing, £3 per session. Freehand Drawing, £1 per term.

The fees for the first two years amount to about £75, and for the remainder of the course for the Associateship they vary from £30 to about £40.

Both the private and the State-aided students are required to furnish themselves with certain instruments and apparatus before the commencement of the courses. These are enumerated in the syllabuses of the several subjects.

Officers of the Army, Navy, and Civil Service, recommended by their respective Departments, are admitted to the Lectures and Laboratories at half the foregoing charges.

Associates of the Normal School of Science or of the Royal School of Mines have the privilege of free admission to the Library and to all the courses of lectures.

Science teachers actually engaged in teaching who are registered by the Science and Art Department as qualified to earn payments for teaching Science may attend any course of lectures on the payment of £1.

Several valuable Exhibitions, Scholarships, and Prizes are attached to the studentship.

Summer Courses for Teachers.—Short courses of instruction are given annually, about July, in different branches of science for the benefit of teachers of science schools in the country. The courses last three weeks. About 200 teachers are admitted to them, and they receive 3rd class railway fare to and from South Kensington, and a bonus towards their incidental expenses of £3 each. (See Science Directory.)

Working Men's Lectures.—Three courses of evening lectures for working men will be given during the session in Mining, Astronomy, and Botany. The admission to each course of six lectures will be 6d. The numbe of tickets is limited by the size of the lecture theatre.

UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

Professor.—H. Ll. Snape, D.Sc. (Lond.), Ph.D. (Gœttingen), F.I.C.

Demonstrator.—A. W. Warrington, M.Sc. (Vic.).

The College is open to male and female students above the age of sixteen years. The Session commences on Saturday, September 28, on which day all Students will be expected to meet the Professors in the Library of the College.

Lecture Courses.—(1) Matriculation Course; two lectures weekly during the Lent and three during the Easter Term. (2) Intermediate Science Pass Course; three lectures weekly during the Lent and Easter Terms. For those Students who have selected Physics or Botany instead of Chemistry at the Matriculation Examination, an Introductory Course of three lectures weekly will be delivered during the Michaelmas Term. (3) Intermediate Science Honours Course; two lectures weekly during the Lent and Easter Terms. (4 and 5) B.Sc. Pass and Honours Courses; each three lectures weekly throughout the Session.

Laboratory Courses.—The Laboratory is open daily from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays. Classes for the Systematic Study of Qualitative and Quantitative Analysis will be formed, and Special Courses will be arranged for those who intend to follow Medicine or Pharmacy, or any one particular branch of Applied Chemistry, always provided that such Students possess the requisite knowledge of Theoretical Chemistry. The hours will be arranged to suit the requirements of the individual Student.

Students intending to proceed to the M.B. or B.Sc. Degree of the University of Edinburgh may count one or two years' residence respectively spent at this College.

Fees.—The Fee for the whole Session, if paid in advance, is £10; if paid by Single Terms, for the first term of attendance in each Session, £4; for the second term, £3 10s.; for the third term, £3. These composition fees enable the Student to attend any or all the Classes of the College, with the exception that a small extra fee is charged for Laboratory Instruction. Thus, for Practical Chemistry, the additional fee is, for six hours' work per week, 10s. per term, and for twelve hours, 20s. per term. The fees for those who desire to spend several days weekly in the laboratory may be learned on application to the Registrar. Fee for a single Lecture Course £1 per term.

Scholarships and Exhibitions varying in value from £10 to £40 per annum will be offered for competition at

examinations which commence on September 18, and exhibitions are awarded at the end of the Session on the results of the class examinations.

New Chemical Laboratories have been recently built in connection with this College and are fitted with every convenience for the prosecution of chemical studies.

UNIVERSITY COLLEGE OF NORTH WALES, BANGOR.

Chemistry.—Professor, James J. Dobbie, M.A., D.Sc. Demonstrator, George McGowan, Ph.D., F.R.S.E.

Physics.—Professor, Andrew Gray, M.A., F.R.S.E. Demonstrator, David M. Lewis, M.A.

The Session opens October 1st, 1889. All regular classes are open to men and women students above the age of 16 years. The following Courses of Lectures will be given.

Matriculation Course.—Subjects: Those prescribed for the London University Matriculation Examination. A class for revision of Matriculation Work will be held during the Summer Term. Fee for the Term, £1 1s.

Intermediate Course.—Elementary Physical Chemistry. Fee for the Term, £2 2s.

B.Sc. Course.—Organic Chemistry. Fee for the Session, £3 3s.

Medical Course.—Inorganic and Organic Chemistry. Fee for the whole Course, £4 4s.

Laboratory Courses.—The laboratory is open on five days of the week from 10 a.m. to 4 p.m. for instruction in Chemical Analysis and in the Application of Chemistry to Medicine and the Industrial Arts. Fees: six hours per week, £1 1s. per Term; twelve hours, £2 2s.; eighteen hours, £3 3s.; twenty-four hours, £4 4s.

Two Courses of Lectures will be given on Agricultural Chemistry. Fee for each Course, 2s.

In November, 1888, the College received a grant of £200 from Parliament for the promotion of Agricultural Education, and a Committee was appointed to frame a complete scheme of Agricultural Instruction for North Wales. Three Dairy Schools in connection with the College have been established in Welshpool, Denbigh, and Bangor, and an Agricultural Department will be opened next session, in which students may receive a complete training in Agricultural Science.

UNIVERSITY COLLEGE OF SOUTH WALES AND MONMOUTHSHIRE.

Professor.—C. M. Thompson, M.A., D.Sc., F.C.S.

Demonstrator.—J. Tudor Cundall.

The Session commences September 30th, and terminates in June, and is divided into three terms.

The Junior Course (delivered during the Michaelmas term only) consists of about 55 lectures, and will cover the subjects prescribed for the London University Matriculation examination. Fee, £2 2s. A revision class is held in the Summer term.

The Intermediate Course consists of 90 lectures in continuation of the Junior Course, and, together with laboratory practice, will cover the subjects required for the Intermediate Examination in Science and the Prel. Sci. (M.B) Examination of the University of London. Fee £3 3s.

The Senior Course includes some 90 lectures devoted to Organic Chemistry; Fee, £3 3s.

An Elementary Organic Course of 10 lectures, and a course of 30 lectures on Qualitative and Quantitative Analysis will also be given.

The Laboratory Course may be modified to meet the requirements of individual students wishing to obtain a special knowledge in some branch of manufacturing or industrial chemistry. Hours, 9 to 1 and 2 to 4.30; Saturday, 9 to 1. Fees—Six hours per week, £3 3s. per session; twelve hours, £2 2s. per term; eighteen hours, £3 3s. per term; twenty-four hours, £4 4s. per term.

Professors Thompson and Parker are recognised by the Universities of Edinburgh, Glasgow, and Aberdeen as teachers in Chemistry and Natural History respectively, so that registered Medical Students can spend one year of their course at the University College, Cardiff. The College is also recognised as an institution at which two years of the course for the degree of Bachelor of Science of the University of Edinburgh may be spent.

Evening Lectures.—A course of Lectures will be given on Elementary Chemistry.

At the entrance examination in September, and the annual examination in June, several scholarships, &c., are awarded. Great importance is attached to special excellence in one subject.

A Hall of Residence for Female Students is attached to the College.

UNIVERSITY COLLEGE, BRISTOL.

Professor of Chemistry.—Sydney Young, D.Sc.

Lecturer.—Arthur Richardson, Ph.D.

The session 1889-90 will begin on October 9. Lectures and classes are held every day and evening throughout the Session. In the Chemical Department lectures and classes are given in all branches of theoretical chemistry, and instruction in practical chemistry is given daily in the chemical laboratory. Excursions to some of the mines, manufactories, and chemical works of the neighbourhood are occasionally made. The department of experimental physics includes various courses of lectures arranged progressively, and practical instruction is given in the physical and electrical laboratory. The Department of Engineering and the Constructive Professions is designed to afford a thorough scientific education to students intending to become engineers, or to enter any of the allied professions, and to supplement the ordinary professional training by systematic technical teaching. This department includes courses specially arranged for students intending to become civil, mechanical, electrical, or mining engineers, surveyors, or architects. Those who attend the mechanical engineering course enter engineering works during the six summer months, and, in accordance with this scheme, various manufacturing engineers in the neighbourhood have consented to receive students of the College into their offices and workshops as articled pupils at reduced terms. Medical education is provided by the Bristol Medical School, which is affiliated to the College. Several Scholarships are tenable at the College. Full information may be obtained of the Secretary.

Day Lectures.

Inorganic Chemistry.

The Course treats of the principles of Chemistry, and of the Chemistry of the Non-Metals and Metals.

Lectures will be given daily at 10 and 11 o'clock.

Organic Chemistry.

This Course will relate to the more important groups of the Compounds of Carbon.

Lectures will be given during the Second Term on Tuesdays and Thursdays at 10 o'clock; during the Third Term on Mondays, Wednesdays, and Fridays at 10 o'clock. Fee, £3 3s.

Practical Chemistry.—Laboratory Instruction.

The Laboratory will be open daily from 10 a.m. to 5 p.m., except on Saturdays, when it is closed. Instruction will be given in the Laboratory in all branches of Practical Chemistry, including Qualitative and Quantitative Inorganic and Organic Analysis, the preparation of Chemical Products, and Inorganic and Organic Research. Special facilities will be afforded to those who desire to study Practical Chemistry as applied to the different processes employed in the Arts and Manufactures, and to Scouring, Bleaching, and Dyeing. The Laboratory is under the immediate supervision of the Professor and the Lecturer. Fees in Guineas—

	5 Days a Week.	4 Days a Week.	3 Days a Week.	2 Days a Week.	1 Day a Week.
Per Session	7½	15	13	10	5
,, Two Terms ..	5½	11	9	7½	4
,, One Term ..	3	6	5	4	2
,, Month	1½	3	2½	2	—

Students may arrange to divide their days of laboratory work into half-days.

Analytical Course.

A Course of Lectures on the Principles of Qualitative Analysis will be given during the First and Second Terms; it is intended to supplement the instruction in Practical Chemistry. All first year's Laboratory Students are expected to attend this Course. The Lectures will be given on Mondays at 10 a.m. Fee, £1 1s. for the two Terms.

Photographic Chemistry.

Instruction will be given in the Photographic Laboratory in Dry-plate Processes, Printing, Enlarging, and in Microscopical Photography, at times to be arranged with those who enter. Fee, £3 3s. for each Term.

Chemical Scholarship.—Among others, a Chemical Scholarship of £25 is offered for competition.

EVENING LECTURES.

This course will consist of Two Lectures a week during the First and Second Terms; they will be devoted to the consideration of the general Principles of Chemistry and Chemical Physics and the Chemistry of Non-Metallic Elements. Special attention will be paid throughout to those products which have a practical application in the Arts and Manufactures.

Fee, 15s. for Two Terms; 10s. for One Term.

Special Courses of Lectures will be given during the First Term on Chemistry as Applied to Soaps and Candles, Mondays, at 8; and during the Second Term on Chemistry as Applied to the Art of Potting, Mondays, at 8.

With the approval of the Council of the Institute of Chemistry students desiring to qualify as Associates may pass through the requisite amount of study at this College, which has also been approved as a centre for the Practical Examination of the Institute.

MASON SCIENCE COLLEGE, BIRMINGHAM.

Professor.—W. A. Tilden, D.Sc. Lond., F.R.S.

Assistant Lecturer.—W. W. J. Nicol, M.A., D.Sc., Edin.

Demonstrator.—Thomas Turner, F.C.S.

The Session will be opened on Monday, October 1st, 1889.

Elementary Course.

Forty Lectures adapted to the requirements of beginners will be given in the Winter and Spring Terms. A Second Course of Twenty Lectures, having reference only to the subjects included in the syllabus of the Matriculation Examination of the University of London, will be given in the Summer Term. Lecture days—Wednesdays and Fridays at 11.30, Thursdays at 3.30.

Persons entirely unacquainted with Chemistry are recommended to attend the first of these Courses before entering for the General Course, which commences in October. Candidates for the Matriculation Examination of the University of London are advised to attend both these Courses.

General Course.

The General Course of Lectures on Chemistry will be found useful by Students who are afterwards to become Engineers, Architects, Builders, Brewers, or Manufacturers (such as Metallurgists, Alkali, Soap, Manure, Glass, or Cement Makers, Bleachers and Dyers, &c.)

Students preparing for the Intermediate Examination in Science and Preliminary Scientific (M.B.) Examination of the University of London should attend the Lectures on Inorganic Chemistry (Winter and Spring Terms).

Candidates for B.Sc. and Intermediate Examinations in Medicine will in general require only that part of the course (Summer Term) which relates to Organic Chemistry.

The full course, extending over three terms, will also satisfy the requirements of Students preparing for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

1. From October to March (Winter and Spring Terms). About eighty lectures on Inorganic Chemistry and Chemical Philosophy will be given on Mondays, Tuesdays, Wednesdays, and Thursdays, at 9.30 a.m. Fee, £5 5s. for the course.

2. April to June (Summer Term). About thirty lectures will be given on Elementary Organic Chemistry, or the chemistry of the most important series of carbon compounds. This course will include all the subjects required for the Intermediate Examination in Medicine of the University of London. Lecture Days—Monday, Tuesday, and Wednesday at 9.30 a.m. Fee, £1 11s. 6d.

An Advanced Course for the study of Theoretical Chemistry and those parts of the subject which are required for the degree of B.Sc. in the University of London will meet once a week. Fee for the session £3 3s.

Laboratory Practice.

The College Laboratory will be open daily from 9.30 to 5, except on Saturdays, when it will be closed at 1 p.m.

Candidates for Intermediate Examination in Science, Preliminary Scientific (M.B.), B.Sc., and Intermediate Examination in Medicine of the University of London, may obtain in the Laboratory of the College the instruction necessary. The three months Course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the Mason College Laboratory. Fees:—

	All day.	Three hours per day.
One Term	7 guineas	4½ guineas.
Two Terms	13 „	8½ „
Threee Terms	18 „	12 „

A Course of short demonstrations and exercises will be given by the Professor or one of his Assistants once a week. All first-year Students will be required to attend, unless exempted for special reasons by the Professor. No Fee.

Metallurgy.—Three Courses of Ten Lectures will be given on the Principles and Practice of Metallurgy. Fee, 10s. 6d. for each course.

Evening Classes.

Several Courses of Evening Lectures are arranged during the Winter and Spring Terms of each session. The subjects are treated in a less technical manner and the fees are nominal.

Excursions.

During previous Sessions permission has been obtained to visit some of the great factories in or near Birmingham, in which chemical and metallurgical industries are carried on. Students have thus had most valuable opportunities of gaining a practical acquaintance with some branches of Applied Science. The privilege thus courteously granted by several manufacturers will, it is hoped, be enjoyed in every future Session. The excursions will be conducted by the Professor.

BRADFORD TECHNICAL COLLEGE.

CHEMISTRY AND DYEING DEPARTMENT.

Professor.—Edmund Knecht, Ph.D., F.I.C.

Demonstrator.—J. R. Appleyard.

Lecturer on Botany and Materia Medica.—William West, F.L.S.

The school year is divided into three terms. The Session began on September 16th and terminates on July 7th. The course of instruction extends over two years, and embraces Lecture Courses on Inorganic and Organic Chemistry, the technology of the textile fibres, mordants, natural and artificial colouring matters, technical analysis, and laboratory practice in analytical chemistry, chemical preparations, and dyeing. Inclusive fee, £4 4s. per term.

During the first and second terms Evening Classes are held for the benefit of persons engaged during the day and for pharmaceutical students.

ROYAL AGRICULTURAL COLLEGE, CIRENCESTER.

Chemical Department.

Professor.—Prof. E. Kinch, F.C.S., F.I.C.

Assistants.—A. G. Bloxam, F.C.S., and W. James.

Systematic courses of Lectures are given on the various branches of Chemistry in its relation to Agriculture, illustrated by experiments, and by the collections in the College Museum. They comprise the laws of Chemical Combination and the general Chemistry of mineral bodies, and of the more frequently occurring bodies of organic origin, with the relationships of their leading groups; and, finally, the applications to practical operations of the Chemistry of the atmosphere, of soils and manures, of vegetation and stock feeding, and of the processes and products of the dairy.

In the Laboratory practical instruction is given in the construction and use of apparatus and in Chemical manipulation and analysis, both qualitative and quantitative. After studying the simple operations and the properties of the commonly occurring substances, the Students are taught to analyse a series of compounds, and apply the knowledge thus obtained to the analysis of manures, soils, waters, feeding stuffs, dairy products, and other substances met with in the ordinary course of Agricultural practice. Chemico-agricultural researches are undertaken by the senior Students under the direction of the Professor and his Assistants.

VICTORIA UNIVERSITY.

THE YORKSHIRE COLLEGE, LEEDS.

Professor of Chemistry.—Arthur Smithells, B.Sc. Lond., F.C.S.

Assistant Lecturers.—C. H. Bothamley, F.C.S., and Herbert Ingle.

The Session begins October 3, 1889.

Lecture Courses.

1. General Course of Chemistry.—Monday, Wednesday, and Friday, at 11.30 a.m., from October to the end of the second term, and during part of the third term. Fee for the Course, £4 4s.

2. Inorganic Chemistry.—First years' Honours Course, Non-metals, Monday, Wednesday, and Friday, at 9.30 a.m.. Fee, £3 13s. 6d.

3. Inorganic Chemistry. — Second years' Honours Course, Metals. Three hours weekly. Fee, £3 13s. 6d.

4. Organic Chemistry.—Tuesday and Thursday at 11.30 p.m] Fee £2 12s. 6d.

5. Theoretical Chemistry.— Advanced Course. Fee, £1 11s. 6d.

6. Chemistry as Applied to Coal Mining.— Tuesday during the First Term, at 4 p.m.

7. Photographic Manipulation.—A Course of Ten Lessons will be given on Fridays, from 2 to 5, during the Third Term, with special reference to dry plate processes and silver and platinum printing. Fee, £1.

Laboratory Courses.

The College Laboratory will be open daily from 9 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it will close at 1 p.m.

Fees for the Session—Students working six days per week, £18 18s.; five, £16 16s.; four, £14 14s.; three, £12 12s.

Class in Practical Chemistry, Saturday mornings, from 9.30 to 12.30. Fee £1 11s. 6d.

Practical Chemistry for Medical Students.—On Tuesday and Thursday, from 10 to 12 a.m., from May to July.

Evening Classes.

A Course of twenty Lectures by Mr. C. H. Bothamley, on the Elements of Inorganic Chemistry (the Non-Metals) will begin during the first and second Terms, on Wednesdays, at 7.30 p.m., beginning October 9. Fee, 10s. 6d.

Dyeing Department.

Professor.—J. J. Hummel, F.C.S.

This Course extends over a period of three years, and is intended for those who wish to obtain a full scientific and practical education in the art of dyeing. It is suitable for those who purpose in the future to take any part in the direction of the operations of dyeing or printing of textile fabrics, *e.g.*, the sons of manufacturers, calico printers, managers, master dyers, &c.

Several valuable Scholarships are at the disposal of the College, viz., the Cavendish, Salt, Akroyd, Brown, Emsley, Craven, and Clothworkers' Scholarships, and the Leighton Trustees' Exhibition.

UNIVERSITY COLLEGE, LIVERPOOL.

Professor.—J. Campbell Brown, D.Sc.

Demonstrators.—C. A. Kohn, B.Sc., Ph.D., and S. G. Rawson, D.Sc.

Assistants.—H. H. Froysell and A. C. Wilson.

The Session commences October 3rd.

The Classes are arranged to suit the requirements of candidates for the Ordinary B.Sc. Degree, for Chemistry Honours, or for the D.Sc. Degree in Victoria University; for Degrees in Medicine of Victoria, London, and Edinburgh; for a special Technological Certificate of University College; and for those studying Chemistry as a preparation for professional, technical, or commercial life. The Classes qualify for the Fellowship of the Institute of Chemistry of Great Britain and Ireland, and other Examination Boards.

Lecture Courses.

General Elementary Course on the principal non-metallic elements and the most important metals, the principles of Chemical Philosophy, and an introductory sketch of Organic Chemistry.

Course A.—Non-metals.

Course B.—Chemistry of the Metals.

Course C.—Organic Chemistry.

Course D.—Physical Chemistry.

Course E.—History of Chemistry and of the Development of Modern Chemical Philosophy.

Course F.—Technological Chemistry: Lectures on Technology are given in connection with Laboratory work at hours to be arranged. The subjects are varied in different years. (1) Alkali and Allied Manufactures. (2) Copper. Iron. (3) Distillation of Coal, and Tar Industries. (4) Fuel. (5) Chemistry Applied to Sanitation. (6) Technical Gas Analysis. (7) Spectroscopy.

Practical Classes.

(1) Junior. (2) Intermediate. Saturday, 9.30 a.m. to 12.30 p.m. Qualitative Analysis of Inorganic Substances and of some of the more common Organic Substances. (3) Special: For the Conjoint Board of Colleges of Physicians and Surgeons. (4) Senior: Practical Organic (Advanced Medical Class). (5) Practical Exercises on Technology, Pharmaceutical Chemistry, Sanitary subjects, Adulterations of Drugs and of Food, Examination of Water and Air, of Animal Secretions, Urinary Deposits, Calculi, and Poisons. (6) Quantitative Class. Course arranged to suit the requirements of the London University B.Sc. Examinations, Pass and Honours, and for Intermediate M.B. Honours.

Chemical Laboratory.

The Chemical Laboratories provide accommodation for every kind of chemical work.

Table of Fees.

Per Week.	One Month.	One Term, Three Months.	Two Terms, Six Months.	Three Terms, One Session.
One day ..	—	£4	£6	£8
Two days ..	—	6	8	10
Three days..	£4	8	10	12
Four days ..	5	9	12	15
Five days ..	—	10	14	18

Students desirous of gaining a thorough theoretical and practical acquaintance with Technical Chemistry, or who intend to adopt Chemical work as a profession, must devote three or four years to special study.

Technological Curriculum.

First Year.—Chemistry, either the Elementary Course or Course A, according to the previous knowledge of the Student. Practical Classes 1 and 2. Mathematics and Mechanics. Engineering Drawing and Design (in this or the following year). French or German. Physics.

Second Year.—Chemistry—Courses A and B; Chemical Laboratory two or three days per week, and the Practical Organic Class during the Summer Term; Technological Chemistry, Course F. Physics, with laboratory work. Mathematics (intermediate), German or French.

Third Year.—Chemistry, Lecture Course on Organic Chemistry, C Lecture Course, E, and Chemical Physics, D. Technological Chemistry, Course F. Chemical Laboratory, four or five days per week. Engineering. The Final Examination for the degree of B.Sc. may be taken if the Student is sufficiently diligent.

Fourth Year.—Courses D and F; part of Course C. Any other Courses omitted in a previous year. Laboratory, five days per week. Students may finally choose a special subject either of research or of applied Chemistry. By spending three years after passing the Preliminary Examination of Victoria University, an able Student may take the B.Sc. Degree in the Honours School of Chemistry.

Evening Classes.

Lectures will be given on (1) Chemistry of the non-Metals; (2) Chemistry of Photography; (3) Fuel.

The Sheridan Muspratt Chemical Scholarship of £50 per annum, tenable for two years, and a Sheridan Muspratt Exhibition of £25 per one year, will be awarded in December on an Examination in subjects which are included in the first two years of the above curriculum. Other Scholarships, Entrance Scholarships, and Free Studentships are also available to Students.

The Laboratory is opened for Students from 10 a.m. to to 5 p.m. daily, on Saturdays from 10 to 1 only.

The Prospectus containing full particulars may be obtained from Adam Holden, 48, Church St., Liverpool, price 6d.; or from the Registrar, University College, Liverpool.

LIVERPOOL COLLEGE OF CHEMISTRY.

Principal.—George Tate, Ph.D., F.I.C., F.C.S.

The Laboratories are open daily from 10 to 5, excepting Saturdays, when they close at 1 p.m. The course of instruction is adapted to the requirements of students of Chemistry as a science, and in its applications to chemical and metallurgical industries. The fee for a three years' course of study is eighty guineas, or per session of three months eight guineas.

Prospectuses, containing full particulars of the day and evening classes, may be had on application at the College.

DURHAM COLLEGE OF SCIENCE, NEWCASTLE-ON-TYNE.

Professor of Chemistry.—P. Phillips Bedson, D.Sc., F.C.S.

Demonstrator—Saville Shaw.

The Session will commence on October 8th, 1888.

Junior Division: First Year Course.—This Course of Lectures will extend over the three terms of the Session, and is intended to serve as an introduction to the Science. The Lectures will be of an elementary character, and whilst framed to meet the requirements of First Year Students will also be serviceable to such as intend pursuing Chemistry in its various applications in the arts and manufactures, as, for instance, Brewing, Metallurgy, the Manufacture of Soda, Soap, Glass, &c. The subjects treated will include an exposition of the Principles of Chemistry, and a description of the preparation and properties of the chief Elementary Substances, both metallic and non-metallic, and their more important native and artificial compounds. The class will meet on Mondays, Wednesdays, and Fridays, at 11 a.m., and will commence on Wednesday, October 17th.

Senior Division: Second Year Course.—A Course about ninety Lectures will be given throughout the Session the subject of which will be Organic Chemistry, or the Chemistry of the Carbon Compounds. This class will meet on Tuesdays and Thursdays, at 11 a m., and will commence on Tuesday, October 15th.

Fee, for either Course, five guineas for the Session.

An Advanced Class will be formed for the study of Theoretical Chemistry. Fee, £2 2s.

A Lecture Course in Analytical Chemistry will be given on Mondays, at 3 p.m., commencing October 22nd. Fee, £1 1s.

Practical Chemistry.—The Laboratory is open from 10 a.m. to 1 p.m., and from 2 to 5 p.m., except on Saturdays, when it closes at 1 p.m. *Laboratory Fees.*—Students working six days per week, £5 5s. per term; alternate days, £3 3s.; one day per week, £1 1s.

Courses of Study.—Students will be divided into two classes:—(1) Regular, or Matriculated Students; and (2) Non-Matriculated Students. Regular Students will be required to follow such a course of study in the subjects professed in the College as will enable them to pass the Examinations for the title of Associate in Physical Science. Non-Matriculated Students will attend such classes as they may select. Every candidate for admission as a matriculated student must pass an examination on entrance, in reading, writing from dictation, English or Latin Grammar, arithmetic (including decimals), and geography. Registered students in medicine are exempted from this examination, or students who produce a certificate of having passed either of the two following examinations:—

1. Durham Examination for certificate of proficiency in General Education, held in March and September.

2. Durham Examination for Students in Arts in their first year, or any examination of a similar nature that may be accepted by the Council.

Associateship in Physical Science.—Every candidate for the Associateship in Physical Science will be required to satisfy the examiners in three, at least, of the four subjects,—Mathematics, Physics, Chemistry, and Geology,—in an examination, to be held at the beginning of his second year.

Exhibitions.—Three Exhibitions of the value of £25, £15, and £10 respectively will be awarded in October next to Candidates desirous of attending the first year course of study in the College.

Evening Lectures.—Courses of Evening Lectures will be given, with a Practical Class for Laboratory instruction.

The examination will be held at the College, and will commence on Monday, October 8th.

Two Exhibitions of £15 each will be awarded at the next examination of "Persons not members of the University," which will be held at Durham in March next.

Several other valuable Scholarships are available for students.

OWENS COLLEGE, VICTORIA UNIVERSITY, MANCHESTER.

Professor and Director of the Chemical Laboratory.—Harold B. Dixon, M.A., F.R.S.

Professor of Organic Chemistry.—C. Schorlemmer, LL.D., F.R.S.

Demonstrators and Assistant Lecturers.—Julius B. Cohen, Ph.D., and George H. Bailey, D.Sc., Ph.D.

Assistant Demonstrators.—A. Harden, Ph.D., and G. Fowler, B.Sc.

The Session begins on October 1, 1889, and ends on June 20, 1890.

The instruction is given by means of Experimental Lectures and Tutorial Classes. The Chemical Classes form part of the Courses for Chemistry in the University.

General Chemistry.

General Chemistry Course.—Tuesdays, Thursdays, and Saturdays, at 9.30, during the two Winter Terms.

Introduction to Organic Chemistry.—Wednesdays and Fridays, at 10.30, during Lent Term.

These courses are intended for Medical Students and others beginning the study of chemistry.

First Year Honour Course.—Mondays, Wednesdays, and Fridays, 3.30 p.m., during the two Winter Terms. The Non-Metals.

Second Year Honour Course.—Mondays, Wednesdays, Fridays, 9.30, during the two Winter Terms. The Metals.

Third Year Honour Course.—Tuesdays, 11.30. Physical Chemistry.

Organic Chemistry (Honours).—Tuesdays, Thursdays, Saturdays, 9.30, during the Session.

History of Chemistry and Chemical Philosophy.—Thursdays, 10.30, during the Session.

Technological Chemistry.

First Course.—Sulphuric Acid and Soda Manufactures. General Principles of Chemical Engineering.

Second Course.—The Chemistry of Fuel. The Manufacture of Illuminating Gas and Gaseous Fuel.

Third Course.—The Chemistry of the Coal Tar Colours.

An ordinary degree of B.Sc. in Chemistry may be taken at the College in either two or three years, according as the student passes the Preliminary Examination on joining the College or whether he takes a year to prepare for that examination. The Degree of B.Sc. with Honours in Chemistry can be taken in three years, and the College Certificate in Technological Chemistry may be taken in the same time.

A number of important Exhibitions, &c., are available to students.

Certificates in Applied Chemistry.

The complete course of instruction extends over four years, and embraces the following subjects:—

First Year (Preparatory).—Chemistry Lectures, General Course:—Chemical Laboratory, two days per week. Pure Mathematics. Elementary Mechanics. Geology. French or German. Geometrical Drawing Lectures (evening class). Mechanical Drawing, Practical (evening class).

Second Year.—Chemistry Lectures, First year Honour classes. Chemical Laboratory, three days per week. Technological Chemistry Lectures. Elementary Physics or Mineralogy Lectures and Practical Courses. German or French. Geometrical Drawing Lectures (evening class). Mechanical Drawing, Practical (evening class).

Third Year.—Chemistry Lectures, Second year Honour. Organic Chemistry Lectures. Chemical Philosophy. Chemical Laboratory, three days per week. Technological Chemistry Lectures (second course). Physical Laboratory, 1 day per week, or Advanced Mineralogy Lectures and Practical Course. Mechanical Drawing, Practical (evening class).

Fourth Year.—Organic Chemistry Lectures. Technological Chemistry Lectures (third year's course). Chemical Laboratory, 4 days per week. Mechanical Drawing, Practical (evening class).

Fees.—Every student is required to pay on admission an entrance fee of £1 1s. and a library fee of 5s., and the fees for the classes for which he enters. As alternative courses are in some instances open to a student offering himself for the Victoria University Examinations, it is not practicable to give tabular statements of the fees for every combination of classes. Special prospectuses may be obtained at the office of the College.

Certificates will be granted to students on the successful completion of this course. Attendance on the full course of four years is expected of candidates for the Certificate, but students may obtain exemption (on cause shown) from the first or the first and second year's courses. Students so excused will nevertheless be required to undergo examination in all the subjects specified. The Certificate will state in which subjects the candidate has gained Honours, and in which he has merely satisfied the Examiners.

UNIVERSITY COLLEGE, NOTTINGHAM.

Department of Chemistry.

Professor of Chemistry—Frank Clowes, D.Sc. Lond., F.I.C., F.C.S.

Demonstrators.—J. B. Coleman, F.I.C., F.C.S., and R. L. Whiteley, F.I.C., F.C.S.

Lecturers.—J. B. Coleman, F.I.C., F.C.S., R. L. Whiteley, F.I.C., F.C.S., C. Haydon White, M.R.C.S., J. W. Carr, B.A., and F. R. Sargeant.

The Classes of the College are open to students of both sexes above sixteen years of age.

The dates of commencement and end of Terms in the Session 1889-90 will be as follows:—First Term, October 7th to December 21st; Second Term, January 20th to April 3rd; Third Term, April 14th to June 28th.

Lecture Courses.—The Chemistry Day Lectures extend over three years. In the first year a student enters for the course on Non-Metals for the first two terms and for Elementary Organic Chemistry in the third term. In his second year he takes the course on Metals for the first two terms, and Advanced Organic Chemistry in the third term. In his third year he attends a course on Applied Chemistry during the first two terms. Fee for Day Lectures and Classes, 50s. for the session of three terms: Non-Metals or Metals 42s.: Organic Chemistry (one term) 21s.: Applied Chemistry, 30s.

Demonstrations and Lectures on Analytical Chemistry will be given in the day and evening, and should be attended by all students.

A Chemical Calculation Class is also held. Fee per Term, 2s. 6d.

Students may qualify themselves by attendance at these lectures and classes for the Examinations of the Universities of London, Cambridge, or Oxford: they may also obtain instruction in Chemistry for technical or other purposes, and can enter for a full Chemical Engineering Curriculum. Special attention is given to the requirements of candidates for the Associateship of the Institute of Chemistry.

Practical Chemistry.—The chemical laboratory is open every day except Saturday from 10 to 5, on Saturday from 10 to 12, and on Tuesday and Thursday evenings from 7 to 9. Each Student works independently of other Students at a course recommended by the Professor. Instruction is given in general Chemical Manipulation and in Qualitative and Quantitative Analysis; and students are enabled to work out the applications of Chemistry to Pharmacy, Dyeing, Agriculture, Brewing, Iron and Steel, Tanning, and other Manufacturing Processes. Fees.—For one term, £6; for the session, £15; for day students for six hours weekly 40s., and 5s. extra for each additional hour per week. For evening students, 10s. for one evening per week, and 20s. for two evenings per week, per term.

Courses of Technical Chemistry Lectures are also given on Dyeing and Bleaching, Brewing, Bread-making, Gas Manufacture, and on other processes of applied Chemistry.

A Pharmaceutical Curriculum extending over three Winter Sessions, includes Pharmaceutical Chemistry (lectures and laboratory work), Pharmaceutical Botany (lectures and class work on specimens), Materia Medica (lectures and use of specimens), and Practical Dispensing, taught by demonstrations and practical work in the laboratory.

Government Lectures and Classes.—Evening Lectures and Laboratory instruction will be given by the Demonrator of Chemistry to Students who intend to present themselves for Examination by the Government Science and Art Department in May next. Inorganic, organic, and practical chemistry, agricultural chemistry, and metallurgy will be taught in the elementary, advanced, and honours stages, each of which commences at the beginning of the College Session in October. Fee for each Lecture Course, 2s. 6d.; for each Laboratory Course, 10s.

Full information concerning all College Classes is given in the College Prospectus.

FIRTH COLLEGE, SHEFFIELD.

Professor of Chemistry.—W. Carleton Williams, B.Sc., F.C.S.

Demonstrator and Assistant Lecturer.—L. T. O'Shea, B.Sc., F.C.S.

The Session will commence on Tuesday, October 1.

First Year's Course.—Chemistry of the Non-Metallic Elements. Monday, Wednesday, Friday, from 10 to 11 a.m. Fee, £3 13s. 6d.

Second Year's Course.—Chemistry of Metals. Tuesday and Thursday, from 10 to 11 a.m. £2 12s. 6d.; or for the First and Second Courses, £5 5s.

Third Year's Course.—Organic Chemistry, on Wednesday, from 9 to 10, and Saturday, from 10 to 11. Fee, £2 2s.; Second and Third Courses together, £4 4s.

A Course of Lectures is arranged for Medical Students, with a special class in Qualitative Analysis.

Laboratory.—Working hours to be arranged between Professor and Students.

Sessional Fees for Day Students:—Six hours per week, £5 5s.; Nine, £7; Twelve, £8 8s.; Eighteen, £11 5s.: Twenty-four, £14; Thirty-two, £17.

Day Students may not enter for less than six hours a week. Students joining the Laboratory at Christmas will be charged two-thirds and at Easter one-third of the Fees for the whole Session.

Fees for short periods (working thirty-two hours per week):—For one month, £3 3s.; two months, £5 5s.

An arrangement has been entered into with the Science and Art Department, South Kensington, which will enable Science Teachers to work in the Chemical Laboratory for twelve hours a week on payment of one-quarter of the usual fee, the Department being willing to pay the remainder under certain conditions, of which full information may be obtained on application to the Registrar.

Evening Classes.—Lectures, Wednesday, 8 to 9. Laboratory instruction, Monday and Wednesday, 6 to 9. Sessional Fee, one evening per week, £1 10s.; two, £3; or Lecture Class and Laboratory, on Wednesday evening, £1 10s.

UNIVERSITY COLLEGE, DUNDEE.

Professor. — Percy F. Frankland, Ph.D., B.Sc., F.I.C., &c.

Lecture Assistant.—Andrew Thomson, M.A., D.Sc.

The seventh session of the College will be opened on October 5th, 1889.

The Lectures and Laboratory practice in Chemistry are recognised by the Royal College of Physicians and Royal College of Surgeons, London, and by the Royal College of Surgeons, Edinburgh, and for degrees in Science and Medicine by the University of St. Andrews and Edinburgh.

The courses are suitable for the Degrees of the London University and for the Civil Service appointments, and will also satisfy the requirements of students in Pharmacy, and of students who intend to become candidates for the Associateship of the Institute of Chemistry, so far as attendance at lectures on General and Theoretical Chemistry is concerned.

Lecture Courses.

The object of these courses will be (1) to give systematic instruction in the general principles of the science, and information regarding the elements and their more important compounds; (2) to show how this knowledge may be usefully applied in the Arts and Manufactures.

A course of instruction in Practical Chemistry in the Laboratory is recommended to all who wish to obtain a sound knowledge of the science, and the methods of applying it to useful purposes—the duration of such course depending upon the special wants of the student.—The Professor will be glad to give any information to intending students.

First year's lecture course: Inorganic Chemistry (Non-Metals), Monday, Wednesday, and Friday, from 10 to 11 a.m.; fee, £2 2s.

Second year's lecture course: 1. Inorganic Chemistry (Metals), Tuesday and Thursday, from 9 to 10 a.m.; fee, £1 11s. 6d. 2. Organic Chemistry, Tuesday, Wednesday, and Thursday; fee, £1 11s. 6d.; fee for the entire year's course, £2 2s.

A Lecture Course on Analytical Chemistry will be given on Saturdays, from 9 to 10. Fee, £1 1s.

Courses of lectures will be given on Dyeing, Bleaching, and the Chemistry of the Textile Fibres, with practical instruction in the Laboratory. In connection with this Department there is an extensive Technical Museum, containing a large collection of specimens illustrating many branches of Applied Chemistry, and particularly the local industries.

Practical Chemistry (Laboratory).

The aim of the Laboratory Courses is to make the student practically acquainted with the science, so that he may conduct chemical analysis and original research, and generally to fit him for applying the science to the Arts, Manufactures, Agriculture, and Public Health. The courses are also suitable for students preparing for their medical and pharmaceutical examinations. A three months' course of Practical Chemistry for the B.Sc., Edinburgh, in the department of Public Health, may be taken in the College Laboratory.

The Laboratory will be open for students daily from 9 a.m. to 4 p.m., except on Saturdays, when it will be closed at 3 p.m. Each student on entering will be allowed to arrange his working hours to suit his own convenience, but will be required to keep the hours when once fixed.

Sessional Fees for Day Students:—The fees for both sessions are—for six hours per week, £3 3s.; each additional hour per week, 10s. 6d. Day students may not enter for less than six hours a week. Students joining the Laboratory during the second term will be charged two-thirds, and during the third term one-third of the above fees. Students may also enter for short periods, working every day in the week at the following fees:—For one month, £2 12s. 6d.; for two months, £5 5s.; for three months, £7 7s.

Evening Classes.—Courses of Lectures and Practical Laboratory instruction.

UNIVERSITY OF EDINBURGH.

Professor.—A. Crum Brown, F.R.S.E.

Two degrees in Science are conferred by the University of Edinburgh, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.). Both these degrees are conferred in Physical and Natural Science, in Public Health, and in Engineering.

Candidates for degrees in Physical and Natural Science must pass a preliminary examination in English, Latin, Arithmetic, the Elements of Mathematics, and the Elements of Mechanics, and in at least two of the following subjects:—Greek, French, German, Higher Mathematics, Natural Philosophy, Logic, and Moral Philosophy.

The First B.Sc. Examination embraces Mathematics, Natural Philosophy, Chemistry, Zoology, including Comparative Anatomy, and Botany. The Second B.Sc. Examination the Higher Mathematics, Experimental Physics, Chemistry, Zoology, Botany, Physiology, and Geology, including Palæontology and Mineralogy.

The D.Sc. Examination embraces Mathematics, Natural Philosophy, Applied Mathematics, Experimental Physics, Practical Astronomy, Chemistry, Zoology and Comparative Anatomy, Animal Physiology, Botany, and Geology, including Palæontology and Mineralogy.

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The main objects of this College are to afford a suitable education to those who wish to qualify themselves for following any industrial profession or trade, and to train teachers for technical schools. It was founded by an Order in Council, dated 26th November, 1886,

according to a scheme framed by the Commissioners appointed under the provisions of the Educational Endowments (Scotland) Act, whereby Anderson's College, the Young Chair of Technical Chemistry in connection with Anderson's College, the College of Science and Arts, Allan's Glen's Institution, and the Atkinson Institution were placed under the management of one governing body.

The Diploma of the College is awarded to Day Students who have attended prescribed courses of instruction and passed the necessary examinations. The ordinary courses extend over three years, but arrangements are made for advanced students continuing their studies in special departments.

The Chemical Laboratory (Prof. Dittmar's) opened on September 2nd. The Lecture Courses commence on October 1st.

Copies of the Calendar for 1889-90 may be had from Mr. John Young, B.Sc., the Secretary, 38, Bath Street, Glasgow, price by post, 1s. 4d.

UNIVERSITY OF ST ANDREWS.

UNITED COLLEGE OF ST. LEONARD AND ST. SALVATOR.

Professor of Chemistry. — T. Purdie, B.Sc., Ph.D., Assoc. R.S.M.

The Session begins on October 29th. A Competitive Examination, open to intending Students of Arts or Science, for nineteen Entrance Bursaries, ranging in value from £30 to £10 each per annum, will be held on Friday and Saturday, October 25th and 26th. Two Degrees in Science are conferred by the University of St. Andrews, viz., Bachelor of Science (B.Sc.) and Doctor of Science (D.Sc.), the regulations regarding which will be found in the "University Calendar."

Lecture Course.

A Lecture is delivered by the Professor of Chemistry, at 11 o'clock, on five days in the week throughout the Winter Session. The Course commences with the study of a few typical substances, forming an introduction to the discussion of Chemical Theory; the Non-metallic and Metallic Elements, with their chief compounds, are then considered; and the latter part of the Course is devoted to Elementary Organic Chemistry. Three Lectures weekly are of an elementary character, and are intended to be useful to Students of Arts who desire to study Chemistry as a branch of general education, or with the view of teaching it in schools; the remaining two Lectures weekly constitute a Supplementary Course, framed so as to meet the additional requirements of Candidates for the Degree of Bachelor of Science and of Medical Students.

Certificates are awarded on the results of separate examinations on the subjects of the general and supplementary Lectures, and the "Forrester Prize" of about £13 is awarded to the best Student of the year.

Fee for the Session, £3 3s.

Laboratory Course.

A class in Practical Chemistry meets for two hours weekly, to which Students attending the Lectures are admitted without additional fee. The Course consists of a series of qualitative and quantitative experiments, designed to give the Student a practical acquaintance with the principles of Chemistry regarded as a subject of general education.

The Laboratory is also open during the Session from 10 a.m. to 4 p.m., for instruction in Chemical Analysis. The fee is £10 10s. for the Session. Shorter Courses of Practical Chemistry will be arranged to meet the requirements of Students who cannot give so much time to the subject, the fees for which vary according to the number of hours taken weekly.

Several free places in the Laboratory will be given to Students desirous of engaging in original work. Applicants must satisfy the Professor that their studies are sufficiently advanced to admit of them prosecuting experimental research.

QUEEN'S COLLEGE, BELFAST.

Professor.—E. A. Letts, Ph.D., F.R.S.E., F.C.S.

I.—*Chemistry.*—The lectures are delivered at 3 p.m., on the first five days of each week until the beginning of April, and on two days of each week after May 1st. The course is divided into three parts:—(1) Chemical Philosophy; (2) Inorganic Chemistry; (3) Organic Chemistry.

II.—*Advanced and Organic Chemistry.*—Lectures on these subjects are given from the beginning of the Session, on Tuesdays and Thursdays, at 10 a.m., until the beginning of April, and at 3 p.m. after May 1st.

III.—*Practical Chemistry.*—In this course the Students are instructed in the general methods of conducting Chemical Analyses.

IV.—*Laboratory Pupils.*—The Chemical Laboratory is open from November until the beginning of April, and from May 1st until the middle of July, on the first five days of the week, from 10 a.m. until 4 p.m. Students are admitted as working pupils on payment of a fee of £5 for the first period, or of £3 10s. for the second period (or for a single term).

QUEEN'S COLLEGE, CORK.

Professor.—Maxwell Simpson, D.Sc., M.D., F.R.S., &c.

The Course of Theoretical Chemistry is divided into Inorganic and Organic Chemistry.

In the first part are discussed the Laws of Combination and Affinity, Molecular Chemistry and Crystallography, and the History of the Non-Metallic and Metallic substances.

In the Organic portion of the Course will be considered the subjects of Organic Analysis, Organic Series, Compound Radicals and Types, Metamorphosis of Organic Bodies, History of Special Animal and Vegetable Bodies.

In treating of the Laws of Chemistry, and the History of Inorganic and Organic Bodies those points will be chiefly dwelt upon which have a practical bearing in the Arts, Medicine, Engineering, and Agriculture. Thence, during the Course, attention will be directed to the application of Chemistry to Medicine and Physiology, to Metallurgic Operations, Chemical Manufactures, Building Materials, Soils, and Manures.

Fee.—For each Sessional Course, £2. Each subsequent Course, £1.

The Chemical Laboratory is open daily except on Saturdays, from 10 to 4 o'clock, under the Superintendence of the Professor, to Students desirous of prosecuting an extended course of qualitative and quantitative analysis, and for the purpose of original investigation in connection with the Arts, or in the higher departments of Scientific Chemistry.

The Course of Practical Chemistry consists of about thirty-nine Lectures, and will commence at the beginning of the Second Term. Fee for each Sessional Course £3.

ROYAL COLLEGE OF SCIENCE FOR IRELAND, STEPHEN'S GREEN, DUBLIN.

Professor of Practical and Theoretical Chemistry.—W. N. Hartley, F.R.S.

The Session commences on Monday, October 7, 1889.

The instruction comprises courses of Lectures on General, Applied, and Analytical Chemistry, and also a course of Lectures on Metallurgy.

The Chemical and Metallurgical Laboratories, under the direction of Professor Hartley, are open every week-day during the Session. Instruction is given in the different branches of Analytical Chemistry, including Assaying, and in the methods for performing Chemical Research. Fee, for the Session of nine months, £12; for six months, £9; for three months, £5; for one month, £2. Fee for a course of assaying not less than £5.

There are four Royal Scholarships of the value of £50 each yearly, with Free Education, including Laboratory Instruction, tenable for two years; two become vacant each year; they are given to Associate Students, not being Royal Exhibitioners, who have been a year in the

College on the results of their examinations. There are also nine Royal Exhibitions attached to the College, of the yearly value of £50 each, with Free Education, including Laboratory Instruction, tenable for three years; three become vacant each year, and are competed for at the May Science Examinations of the Department of Science and Art.

A Diploma of Associate of the College is granted at the end of the three years' course.

Evening Classes.—Courses of Evening Lectures are occasionally given by the Professors during the Session.

CHEMICAL LECTURES, CLASSES, AND LABORATORY INSTRUCTION.

City and Guilds of London Institute for the Advancement of Technical Education.—*Central Institution, Exhibition Road.*—Professor of Chemistry, H. E. Armstrong, Ph D., F.R.S. The object of this Institution is to give to London a College for the higher technical education, in which advanced instruction shall be provided in those kinds of knowledge which bear upon the different branches of industry, whether Manufactures or Arts. The main purpose of the instruction given in this Institution is to point out the application of different branches of science to various manufacturing industries. In order that this instruction may be efficiently carried out, the Institution, in addition to the lecture theatres and class rooms, is fitted with laboratories, drawing offices, and workshops; and opportunities are afforded for the prosecution of original research, with the object of the more thorough training of the students, and for the elucidation of of the theory of industrial processes. The courses of instruction are arranged to suit the requirements of—1. Persons who are training to become Technical Teachers; 2. Persons who are preparing to enter Engineers' or Architects' offices, or Manufacturing works; 3. Persons who desire to acquaint themselves with the scientific principles underlying the particular branch of industry in which they are engaged. The Matriculation Examination will be held on Monday, September 23rd. *Technical College, Finsbury.*—Professor of Chemistry, Raphael Meldola, F.R.S. The operations of the Technical College, Finsbury, are divided into two distinct portions: Day Classes for those who are able to devote one, two, or three years to systematic technical education; Evening Classes for those who are engaged in industrial or commercial occupations in the daytime and who desire to receive supplementary instruction in the application of Science and of Art to the trades and manufactures in which they are concerned or employed. The College embraces the following departments:—1. Mechanical Engineering and applied Mathematics; 2. Electrical Engineering and Applied Physics; 3. Industrial and Technical Chemistry; 4. Applied Art; 5. the Building Trades. The College is under the general direction of the Principal. Each Professor is assisted by Demonstrators. Besides these there are Lecturers and Teachers in special subjects. The Instructors in the workshops are skilled craftsmen. All the Teachers of the Trade Classes are men who have worked at their industry as foremen. The Session is divided into three terms:—The Winter term commences on Tuesday, October 8th. An examination for the admission of Students will be held at the College at 10 o'clock on Wednesday, October 2nd, 1889, and the work of the Session will commence on October 8th.

Birkbeck Literary and Scientific Institution, Bream's Buildings, Chancery Lane.—*Chemistry:* Courses will be conducted, commencing October 1st, adapted for the Elementary, Advanced, and Honours Examinations of the Science and Art Department, and for the Matriculation, B.Sc., and M.B. Degrees of the London University. *Inorganic Chemistry:* Mr. G. Chaloner, F.C.S. Lectures—Elementary, Tuesdays, 8.30 p.m.; Advanced, Thursdays, 7 p.m.; Practical, Tuesdays, 6—8 p.m.; Thursdays, 8—10 p.m.; Saturdays, 7—9 p.m. *Organic Chemistry:* Mr. F. Gossling, B.Sc. Lectures—Elementary, Wednesdays, 7.30 p.m.; Advanced, Wednesdays, 8.45 p.m.; Practical, Wednesdays, 6—7.30 p.m.; Fridays, 6—10 p.m.

School of the Pharmaceutical Society of Great Britain, 17, Bloomsbury Square, London, W.C.—Professor of Chemistry, Wyndham R. Dunstan, M.A., F.C.S. Professor of Practical Chemistry, John Attfield, Ph.D., F.R.S. In this school, which is specially intended for Pharmaceutical Students, Courses of Instruction are given in the sciences of Chemistry (Physical, Inorganic, and Organic) and Botany, as well as in their applications to Pharmacy and Medicine. Professor Dunstan delivers during the Session (October to July) two Courses of Lectures on Chemistry; an Elementary Course from October to April and an Advanced Course from April to July. The Laboratories for practical instruction in Chemistry under the direction of Professor Attfield are open daily throughout the Session. The Research Laboratory of the Society, under the direction of Professor Dunstan, is open without payment to properly qualified persons who are desirous of conducting pharmacological and chemical investigations. Particulars respecting Scholarships, Medals, and Prizes, as well as other information relating to the School, may be obtained on application.

Charterhouse Science and Art Schools.—The Winter Session will commence on Saturday, September 28th, 1889, under the presidency of the Rev. H. Swann, M.A. Classes are established in this institution by which instruction of a practical character is given in most of the Sciences at a very nominal fee; whilst in Art, at an equally low rate, Students, under the direction of five competent instructors, can be advanced in their studies. Those who have leisure can, at a very moderate charge, attend the Day Classes in Art. Day Classes will also be held to prepare Candidates for Matriculation (Lond.), the Clerical, Medical (including Dental), Legal, and other Examinations. Students who aim at becoming proficient in Chemistry (Organic and Inorganic) have the opportunity of working in a well-fitted Laboratory, capable of accommodating sixty Students. Aspirants for University Honours can at a small expense be assisted in their studies.

The City School of Chemistry and Pharmacy, 27, Chancery Lane, London, W.C.—Principal, Mr. Maurice Williams. Theoretical and Practical Chemistry, Chemical Physics, Theoretical and Practical Pharmacy, Materia Medica, and Therapeutics.

New Central School of Chemistry and Pharmacy, 173, Marylebone Rd., London.—Mr. J. Woodland, F.C.S., Lectures are given on Chemistry, Botany, Materia Medica, Pharmacy, Latin, and Physics. Laboratory instruction.

South London School of Pharmacy, 325, Kennington Road, S.E.—This School opened on September 16th, and the Session lasts until July 15th, 1890. Lectures on Chemistry and Physics, by Dr. John Muter, F.R.S.E., F.I.C., Daily, at 9 a.m. (Organic) and 10 a.m. (Inorganic). Lectures on Botany daily at 12 noon, and at 2 p.m. on Materia Medica and Pharmacy, by Mr. Dodd, F.C.S. The Laboratories for Qualitative and Quantitative Analysis open daily from 9 till 5, under the direction of Mr. de Koningh, F.I.C., F.C.S, assisted by Mr. Armstrong. The Students' Laboratory of this Institution is specially designed to accommodate 40 Students. The Technical Laboratory is open daily from 9 till 4, and is fully fitted with all apparatus for teaching the manufacture of drugs and chemicals. Periodical Examinations of the Students are held by Visiting Examiners appointed by the Council of Education, and Medals and Certificates are awarded on the results thereof. Fees for the first three months £10 10s. (junior) and £12 12s. (senior); afterwards £2 2s. and £3 3s. per month respectively, inclusive of all departments.

Polytechnic Institute, 309, Regent Street, London, W.—Special Courses of Lectures on (*a*) the Manufacture of Painters' Oils, Colours, and Varnishes; and (*b*) Oils and Fats, including Candle Manufacture, will be delivered on Tuesday Evenings during the winter by Mr. J. G. McIntosh, commencing on Tuesday, October 1st, at 8 p.m. Classes for practical instruction in these subjects under the immediate superintendence of the Lecturer will also be formed. For further particulars apply to Secretary.

Onslow College of Science, 183, King's Road, Chelsea, S.W.—Lectures and Laboratory instruction in Chemistry and Pharmacy. Special Evening Classes in Inorganic and Organic Chemistry, Metallurgy, &c. The Chemical and Metallurgical Laboratories are open every day and evening for practical work. Principal, Mr. W. H. Martin.

Royal Victoria Hall, Waterloo Bridge Road, S.E.—Science and Technical Classes, Session 1889-90. Lectures will be given in the following subjects:—Principles of Chemistry, Electricity and Magnetism, Heat, Light, and Sound, Biology, and Mechanics. The instruction given is suited to artizans and practical men, and is chiefly in connection with the Science and Art Department, South Kensington.

Portman School of Pharmacy, 156, Marylebone Road, Regent's Park.—Principal, Mr. F. H. Painter.

University Correspondence College, 1, Strand Hotel Buildings, Booksellers Row, W.C.—Specially prepared Courses of Lessons are given for the Examinations of the University of London.

Westminster College of Chemistry and Pharmacy, Trinity Square, Borough, S.E. — Messrs. Wills and Wootton.

Bristol Medical School.—Mr. T. Coomber, F.C.S.

Institute of Chemical Technology, Hackins Hey, Liverpool.—Principal, Mr. A. Norman Tate, F.I.C. The course of instruction is intended more especially for students who wish to gain a knowledge of chemistry and the allied sciences in their relation to industrial and commercial pursuits, and embraces a thorough preliminary course of theoretical chemistry and practical laboratory work, followed by instruction in chemical technology fitted to the requirements of each pupil. In addition to these chemical studies, students who desire it can enter upon a special course calculated to afford them knowledge useful in the erection and arrangement of manufactories and plant, and construction of apparatus.

Leeds School of Medicine.—Prof. Smithells.

Leeds School of Science and Technology.— Mr. J. Wertheimer, B.Sc., F.C.S., and Mr. E. Rawlins, F.C.S. Day Classes for ladies and gentlemen in Practical Chemistry and in Chemical Physics.

Manchester Technical School. — Lecturers: Dr. Gibson Dyson, F.C.S., Mr. E. Bentz, F.C.S., and Dr. T. T. Best. The day classes commenced on Sept. 2nd, 1889, and the evening classes will commence on Sept. 23rd. The school is equipped with two large laboratories for the practical study of Pure Chemistry and Physics, a Laboratory for Metallurgy, and one for Dyeing, Bleaching, and Printing. Special practical work in any branch of Chemical Technology, or in preparation for University Examinations, will be arranged to suit individual Students. The Evening Courses of instruction are esgecially designed to meet the wants of those already engaged in various industries. A syllabus, containing full particulars as to hours, fees, &c., may be obtained from Mr. J. H. Reynolds, The Technical School, Manchester.

Newcastle-on-Tyne School of Science and Art and Technical College (Chemical and Metallurgical Department).—Principal, P. Hawkridge, B.A. Lecturers and Demonstrators, W. D. Oliver, F. N. Cook, H. Oliver, J. D. Best, W. Carr, and J. P. McVie.

Institute of Science and Art, Municipal Buildings, Reading.—Head Science Master: Alfred J. Shilton, F.C.S. Session begins first week in October.

Sheffield Borough Analysts' Laboratory, 1, Surrey Street. — Mr. A. H. Allen, F.C.S. Day and Evening Classes.

Sheffield Mechanics Institution, Tudor Street.—Lecturer on Chemistry, Henry J. Hardy, F.C.S., &c. The Course is divided into Organic and Inorganic Chemistry. About 30 Lectures are given in each. The Session commences September 26th.

Public Laboratory, 34, Bank Street, Sheffield.—J. O. Arnold, F.C.S., and Henry J. Hardy, F.C.S. Day and Evening Classes. Special Classes in Iron and Steel Analysis.

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THE CHEMICAL NEWS.

Vol. LX. No. 1557.

ADDRESS TO THE CHEMICAL SECTION OF THE BRITISH ASSOCIATION.*

By Sir LOWTHIAN BELL, Bart., F.R.S., F.C.S., D.C.L., M.Inst.C.E., President of the Section.

It has occasionally been the practice of former occupants of this chair to devote a considerable portion of the presidential address to the more recent discoveries in chemical science. This branch of learning advances now with such rapid strides and covers so wide a field, that no one who has not made it the business of his life can hope to discharge this duty with even a moderate share of success.

My immediate predecessor, indeed, discouraged any further attempts in this direction on the ground of the impossibility of doing it justice within the limits of a short discourse, and his remarks were consequently directed to the best methods of teaching the science with which Section B is more directly concerned. I propose this morning to add my testimony to the importance of Dr. Tilden's recommendation, by comparing the rate of progress of one of our great national industries as it has been advanced with and without the aid which chemistry is capable of affording. For this purpose I have selected the metallurgy of iron, not only from my greater familiarity with its details, but because, in my judgment, it affords a suitable example for the object I have in view.

It is needless to insist on the disadvantage attending the application of a science to practical work, without a fair knowledge of the principles which regulate its action. At the same time it would be unfair to those who were engaged in the manufacture of iron during the first half of the present century to deny the value of the services rendered to their art, without giving much thought to the laws of nature upon which their processes depended. The work so performed sufficed, nevertheless, to place the world in possession of the metal in such abundance and at so low a cost that no engineering works have been delayed on account of the high price of or absence of the required quality in the produce of our ironworks during the period in question. On the other hand, it is not to be denied that since the iron-masters have allied themselves with the chemist they have made more progress in thirty years than their predecessors did in three centuries.

No one unacquainted with the archæology of the iron trade could suppose that the colossal furnaces pouring forth their streams of molten metal, followed by the rapid action of the Bessemer Converter, were the modern representatives of the iron-making appliances of former days. Out of the latter, in a low hearth not larger than a domestic fireplace, often dependent on the wind for their blast, a few pounds of ore were at a considerable cost for labour, fuel, and waste of metal, converted into malleable iron. By means of a modern furnace, in an hour and a half a ten-ton converter can be filled with liquid cast-iron, which in twenty minutes may be run into ingots cheaper, stronger, and more malleable than the best wrought iron of our ancestors, or indeed of our own manufacture.

How out of the small fire of the ancient ironworks the German Stück-Ofen was evolved is a matter of conjecture. In both, owing the conditions under which the fuel was burnt, carbon dioxide was largely the product of its combustion. The oxidising property of this gas was in each the cause of the waste of metal just spoken of. Probably, and for other reasons than avoiding this loss of iron attempts were made to increase the dimensions of the Stück-Ofen. If this addition were one of limited extent, the smelter would find, to his cost, that a substance was obtained which no longer possessed the malleable property of that obtained from the lesser furnace. This change would be due to the absorption of carbon, but not in sufficient quantity to constitute that valuable form of the metal known as cast-iron. With a material useless for the smith and incapable from its difficult fusibility of being run into moulds, we can understand the delay which took place in the introduction of the blast furnace which about the middle of the sixteenth century gave to cast-iron a recognised and valuable position in the arts.

In those days there was no very exact science to appeal to, for two hundred and fifty years after the "high furnace" of the Germans and French had been set to work, Fourcroy in his "General System of Chemical Knowledge and its Application to the Phenomena of Science and Art," arrived at the conclusion that cast metal was erroneously supposed to be a mixture of slag and iron or a compound of arsenic or manganese and iron. This was written in 1804 in a work of five thousand pages, when he leant to the opinion that Monge and Berthollet were more correct in considering the product of the blast furnace as consisting of iron, oxygen, and carbon.

When the malleable iron-maker had placed in his hands a material containing, as the pig did, more than 90 per cent of metal, he found it greatly to his advantage to avoid having to deal with all the earthy matter contained in the ores, for it was the presence of silica and alumina which helped to add to the waste incurred in the old hearths. The object sought for in the old Catalan fires, as they were called, in treating ore was one of a reducing or deoxidising character, whereas the reverse of this was required when ore was replaced by pig-iron. In the first, oxygen had to be removed from the oxide of iron, in the latter oxygen had to be united with the metalloids found in the pig. These were distinctions unknown in the days we are considering, and therefore did not trouble the minds of the iron-masters. In both cases there was a large formation of oxide of iron, and when pig-iron was handed over to the Catalan furnace man, it was the oxide of iron so generated which performed the desired duty, and thus this simple mode of procuring malleable iron remained undisturbed for upwards of two hundred years.

The discovery which led to the discontinuance of the low blast furnace as a means of procuring iron in its malleable form was that of puddling made by Cort in 1784. In point of fact Cort's process was merely doing in a reverberatory furnace that which was previously effected by means of compressed air. In an economic point of view, however, the difference is great, and its consequences were of immense importance; for to the puddling furnace we were first indebted for an ample supply of cheap iron by which, in a variety of well-known ways, the interests of the human race have been so largely promoted. As an indication of the indifference of those formerly engaged in industrial pursuits to the scientific aspect of their calling, may be mentioned the fact that puddling had been largely followed for upwards of half a century before it occurred to anyone to examine the chemistry of the process.

Down to the beginning of the seventeenth century the only fuel used in the blast furnace, and, indeed, in the manufacture of iron generally, was charcoal. In 1620 Dudley made several attempts to substitute mineral coal for vegetable fuel in his smelting works, which, by the exhaustion of timber, had become very expensive. He failed in this, and in consequence the British iron trade gradually fell until it was not equal to the production of one modern blast furnace. This happened in 1740, when Darby, by treating pit coal in the same fashion as the charcoal burners had done with wood, *i.e.*, by charring it,

* Read Thursday, September 12 1889

restored vitality to an expiring industry. It is true the restoration must have been of a languid character, for in half a century afterwards it is said the weekly produce of a furnace did not exceed fifteen or sixteen tons.

Various changes were introduced into the manufacture of iron in the first quarter of the present century, but these were rather of a mechanical than of a chemical nature. They chiefly owed their origin to the lessons taught by the chemist Black to James Watt, who profited by them in the application of steam as a motive power. This brings us to the year 1828, a year which will always be distinguished in the annals of the iron trade, by the discovery of Neilson of the value of heated air in smelting the ores of this metal. I never heard it pretended that this inventor had any pretensions to be considered a man of science. Had it been otherwise, the knowledge of the virtues of the hot blast might have been indefinitely postponed, and this opinion is founded on the fact that for many a long year no satisfactory explanation was given why heat obtained by burning coal in the hot air apparatus was capable of saving three or four times its weight in the fuel consumed in the furnace itself. I propose, with your permission, to consider this subject with more attention than I shall devote to other portions of this address, and I am led to do this, not only because it is one of some scientific interest, but because its study seems to afford a solution to some questions in respect to which great differences of opinion prevailed among those whose daily work led them to pay much attention to their details. These questions have all a reference to the quantity of fuel consumed in smelting the ore, as this may be affected by the temperature of the blast and the dimensions of the furnaces employed for this purpose.

As is well understood, the heat excited in an iron furnace may be classified under three heads:—

First, that derived from the combustion of the coke at the point where the blast enters the furnace, the ultimate product being carbonic oxide.

Second, the conversion of a portion of this carbonic oxide into carbon dioxide.

Third, the heat carried into the furnace by the blast.

For the better illustration of the relations which the heat derived from these sources bear to each other, a table (No. I.) has been prepared in which the quantities of each are given in centigrade calories, and reckoned upon 20 units of iron to correspond with English weights. The information upon which the calculations are based is derived from actual observation gathered from furnaces of different sizes and fed with air at different temperatures.

A second table contains statements showing the manner in which the heat so generated is appropriated in the various divisions of the duty the furnaces had to perform, and, for facility of comparison, alongside the quantities of heat so required, their equivalents in the coke used have been added.

In the table, No. II., the appropriation of the heat is separated into *Constants* and *Variables*. The first consists of items where the quantity of heat in making a particular quality of iron is only liable to alterations of trifling amount. On the other hand, the variables exhibit in A and B differences so considerable that work which in in the furnace blown with cold air absorbed 73,388 calories per 20 cwts. of pig-iron was done with 58,645 calories by merely raising the blast to 485°.

The cause of this great variation in the amount of heat required for a given weight of pig-iron, produced under different circumstances as to temperature of blast and size of furnace, depends on changes in the actual amount of work to be performed. How this arises will be best seen in the description of the four examples set forth in the two tables.

Beginning with A, which is a furnace 48 feet in height, blown with cold air, and consuming 45 cwts. of coke and 18 cwts. of limestone per ton of metal, the volume of gas produced may be taken at 14,460 cubic yards at ordinary

Table I.

—	A	—	—	—
Height of furnace in feet ..	48	48	80	80
Calories—per unit of coke burnt to CO	2078	2028	2018	2045
Calories from portion of this CO burnt to CO_2	560	1059	1636	1463
Total calories from coke ..	2638	3087	3654	3508
Calories in blast	—	508	534	732
Total heat per unit of coke..	2638	3595	4188	4240
Temperature of blast C. ..	0°	485°	485°	695°
Cwts. blast per ton of metal	228	128	103	94
Cwts. escaping gases per ton of metal	285	170	138	126
Cwts. slag per ton of metal..	34	31	29	28

temperatures and pressures. At the temperature at which they escape we may assume the volume per ton of iron to be about 36,000 cubic yards, passing out of the furnace at the rate of 357 cubic yards per minute.

In comparing the consumption of coal formerly burnt in the hot-air stoves with the saving of coke in the furnace, account must be taken of the different conditions of the combustion. In Table I., owing to the small quantity of carbon dioxide formed, the heat evolved is only 2638 calories per unit of coke, whereas each unit of the coal consumed in heating the air afforded three times this quantity of heat. Doubtless there was a great loss in the operation of heating the air, for it would not appear that much above one-fourth of the theoretical quantity of heat capable of being generated by the coal reached the furnace through the tuyères.

We have now to consider the nature of the change which is effected in a furnace where, for every 2638 calories generated by the combustion of the coke, 508 calories are carried in by the blast. It will be readily understood that with the velocity at which the gases are passing out of the cold-blast furnace they have but little time to impart their heat to the incoming solids, or to have the carbonic oxide they contain converted into carbon dioxide. The withdrawal of so much coke, and its place taken by heat contained in the blast, means that the 14,460 cubic yards of escaping gases are reduced to about 12,120 cubic yards. The effect of this is not only to alter the speed at which the gases are passing through the materials, but to alter the relation in point of quantity which the ironstone present in the furnace bears to the coke, so that in point of fact a larger space is occupied by the ore than was before, and a lesser one by the fuel. We have thus the carbonic oxide passing more slowly over the oxide of iron at the same time that there is a greater quantity of the oxide exposed to the influence of the reducing gas. To illustrate how this operates, a table has been prepared showing how each 1000 cubic feet of furnace space is occupied in the four cases we are considering:—

	A. 48 feet cold blast.	B. 48 feet hot blast.	C. 80 feet blast.	D. 80 feet blast.
Coke cubic ft. ..	736	686	590	590
Limestone ,, ..	63	75	86	77
Ironstone ,, ..	201	239	324	333
	1000	1000	1000	1000

The immediate effect of the introduction of the hot blast is to alter the spaces filled by the three minerals from those given in Column A to coke 686, limestone 75, and ore 239 cubic feet. This is followed by a twofold advantage. Volume for volume, ore and limestone possess double the heat-intercepting power of coke, and there is 19 per cent more ore ready to oxidise the carbonic oxide passing over it at a reduced speed of 16 per cent than there was when using cold air. The increased efficiency of the coke, due to a more perfect cooling of the gases and higher oxidation of the carbonic oxide, permits

Table II.

Showing the appropriation of Heat and its equivalent per ton Iron.

Appropriation of heat per 20 of pig-iron.	A—Blast 0° C.		B—Blast 485° C.		C—Blast 485° C.		D—Blast 695° C.	
	Calories.	Cwts. coke.	Calories.	Cwts. coke.	Calories.	Cwts. coke.	Calories.	Cwts. coke.
CONSTANTS:—								
Reduction of Fe_2O_3 in ore	33,108	12·550	33,108	9·209	33,108	7·905	33,108	7·808
Reduction of metalloids in pig ..	4,174	1·582	4,174	1·161	4,174	0·996	4,174	0·984
Dissociation of CO ($2CO = C + CO_2$	1,440	0·546	1,440	0·400	1,440	0·344	1,440	0·340
Fusion of pig-iron	6,600	2·501	6,600	1·836	6,600	1·576	6,600	1·557
Constant calories per 20 of pig ..	45,322	—	45,322	—	45,322	—	45,322	—
Coke consumed per 20 of pig. Cwts.	—	17·179	—	12·606	—	10·821	—	10·689
VARIABLES:—								
Evaporation of water in coke.. ..	630	0·239	411	0·114	312	0·074	298	0·070
Decomposition of water in blast ..	5,420	2·055	3,348	0·931	2,720	0·649	2,408	0·568
Expulsion of CO_2 in limestone ..	6,660	2·526	5,920	1·647	5,054	1·207	4,070	0·961
Reduction of CO_2 in limestone to CO	6,912	2·620	6,144	1·709	5,248	1·254	4,099	0·962
Fusion of slag	18,590	7·045	17,325	4·819	16,720	3·993	15,565	3·673
Carried off in escaping gases.. ..	29,482	11·178	18,486	5·144	11,043	2·636	8,906	2·101
Heat in tuyere water at hot-blast furnaces, loss from walls, &c. ..	5,694	2·158	7,011	1·950	7,057	1·686	9,389	2·216
Variables for 20 of pig	73,388	—	58,645	—	48,154	—	44,735	—
Variables for coke for 20 of pig ..	—	27·821	—	16·314	—	11·499	—	10·551
SUM OF CONSTANTS AND VARIABLES:—								
Calories for 20 of pig-iron	118,710	—	103,967	—	93,476	—	90,057	—
Cwts. of coke for 20 of pig-iron ..	—	45	—	28·92	—	22·32	—	21·24

Table III.

Showing the quantity of Oxygen and Carbon in gases per 1000 parts of Pig-iron produced. The eight feet immediately below charging plates is occupied by charging apparatus.

Distance below top of minerals.	0 ft.		8½ ft.		18 ft.		31 ft.		44¼ ft.		57 ft.		62½ ft.		68 ft.	
	O.	C.	O.	C.	O.	C.	O.	C.	O.	C.	O.	C.	O.	C.	O.	C.
No. 1. Oxygen ..	1843	—	1250	—	1235	—	1234	—	1236	—	1207	—	1137	—	1348	—
Carbon ..	—	1101	—	864	—	816	—	871	—	904	—	899	—	890	—	967
No. 2. Oxygen ..	1843	—	—	—	1410	—	1482	—	1190	—	1207	—	1255	—	1366	—
Carbon ..	—	1104	—	—	—	914	—	1046	—	894	—	887	—	—	—	927
No. 3. Oxygen ..	1670	—	1309	—	1206	—	1312	—	1256	—	1253	—	1253	—	1378	—
Carbon ..	—	1048	—	926	—	907	—	918	—	946	—	931	—	939	—	1013
No. 4. Oxygen ..	1670	—	1271	—	1224	—	1300	—	—	—	1261	—	1285	—	1387	—
Carbon ..	—	1048	—	897	—	898	—	917	—	—	—	926	—	977	—	1021

Note.—Nos. 3 and 4 were using partially calcined limestone, hence the deficiency of O. and C. until the lower depths are reached.

Table IV.

Showing what may be regarded as a typical instance of the absence of Carbon Dioxide in the gases taken from a furnace of 80 feet. Measurements taken from the highest level of the minerals, *i.e.*, eight feet below charging plates.

Depth below charge.	Escape pipe.	3½ ft.	9 ft.	16 ft.	22½ ft.	28¾ ft.	35 ft.	41¾ ft.	66 ft.
Carbonic Acid	16·07	11·71	10·03	8·17	6·12	—	—	0·72	3·01
Carbonic Oxide	27·34	29·71	31·39	31·40	32·79	35·27	36·00	36·02	39·47
Hydrogen	0·11	0·10	0·07	0·14	0·28	0·10	0·11	0·08	0·14
Nitrogen	56·48	58·48	58·51	60·29	60·81	64·63	63·89	63·18	57·38
Total ..	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00	100·00

its further suppression until the relative spaces filled by the materials are those shown under Column B. These advantages would not of themselves suffice to save 16 cwts. of coke, or thereabouts, out of 45 cwts., but the reduction in the coke consumed is followed by a diminution in the quantity of air used, and in the weight of gases and slag produced. A reference to the appropriation of heat classified under the head of Variables will show in consequence diminution from 73,338 to 54,643 calories.

It may be asked whether this prolonged exposure of the ore to the reducing gases could not be secured by driving the furnace at a lower speed. There is, however, a point which may be regarded as one of equilibrium, in which the quantity of cold materials charged at the top just suffices to reduce the temperature of the gases, leaving it as far as is possible consistent with the dimensions of the furnace. If the volume of blast entering at the tuyères is lowered one-half it would mean that the materials would be exposed for twice the time to the hot gases they were previous to the alteration in the rate of driving. The elevation in the temperature of the coke would enable its carbon to act on the carbon dioxide, so that there would ensue as great a loss under the second head of heat evolution in Table I. as there is gained by a more perfect interception of the heat contained in the gases.

There is, however, another way of securing this prolonged exposure of the ore to the action of the reducing gas without incurring the inconvenience just referred to, viz., by increasing the dimensions of the furnace blown with cold air. When this was done by raising the height from 48 to 71 feet it was found that the duty performed by the coke, apart from the heat contained in the blast, was just about the same as that in the hot-blast furnace.

With regard to the position of equilibrium above referred to, it is worthy of remark that, while this was reached when a furnace of 48 feet ran 100 tons per week when driven with cold air, it was not arrived at in one of similar dimensions using heated air until the make was increased to about 220 tons.

When we proceed to examine the composition and weight of the gases given off by a 48-feet furnace blown with air at 485° C., it will be found that about 20 per cent of the carbon as dioxide has disappeared, due no doubt to the still excessive temperature of the upper zone and too rapid a current of the reducing agent. An obvious way to remedy this evil would be by an addition to the capacity of the furnaces. This was done by raising them to a height of 80 feet, with a cubical space three or four times greater than those of 48 feet. In such a furnace almost the full theoretical quantity of carbon as dioxide has been obtained, but, while the larger furnace held three or four times as much ore, &c., the production was only about double that of the lesser. On referring to Table II. it will be seen that a further economy of 6·6 cwts. of coke has been effected in Furnace C as compared with B, due solely to an enlargement of space, for the temperature of the blast was exactly the same in both. This improvement, it will also be perceived, is due to an extension of those causes which acted so beneficially when hot air was applied to B.

If 6·6 cwts. of carbon, or thereabouts, is the full quantity per ton of iron which can be found in the gases as dioxide, and if, in a furnace working under the conditions of C, it requires 22·32 of coke to furnish this carbon and that in the carbonic oxide, it is clear we cannot withdraw any coke without disturbing the position of equilibrium supposed to have been established in the case of the furnace in question. Suppose into such a furnace the blast, instead of 485°, is admitted at 695° as happened under Column D. The additional heat, 732 calories, instead of 534 as in C, will make itself felt throughout the entire height of the furnace, including, of course, the upper zone. Immediately this happens the carbon dioxide generated by the reduction of the ore attacks the coke and escapes as carbonic oxide. If Table I. is examined it will be seen that almost the whole of the additional heat carried into the furnace D, as compared with C, has been absorbed by the disappearance of carbon dioxide, so that the net power of the coke unit in both cases is practically the same. Nevertheless it will be remarked that there is still a small saving of coke due to a reduced amount of blast, escaping gases, &c.

From what has preceded it has been concluded that a furnace of 80 feet affords sufficient opportunity for the gases being as fully saturated with oxygen as the nature of the process of deoxidising the ore will permit. The sensible heat in the escaping gases, however, still represents a considerable loss, reduced as they have been from 29,482 to 11,043 calories.

According to estimate it was believed that the reduction of oxide of iron ought to be attended by an increase of temperature—in other words, the conversion of carbonic oxide into carbonic dioxide produced more heat than that absorbed by splitting up oxide of iron into its constituent parts. The estimated difference not being a large one, an experiment was made by substituting in the furnace inert substances having about the same specific heat as the ore. The results confirmed the correctness of the calculation—the temperature of the escaping gases fell, and rose to their normal point when the use of ore was re-commenced. A more expensive experiment was subsequently made in the same direction by building, at Ferryhill, a pair of furnaces having a height of 103 feet, without any substantial benefit being derived from the large additional expenditure incurred.

It was Scheerer, I think, who first divided the blast furnace into zones. The first division, beginning at the top and extending twelve feet downwards, was designated the preheating zone; the following eighteen feet downwards was distinguished as the reducing zone; the next eight feet the carburising zone, followed by four feet which constituted the zone of fusion. The lowest of all, having a depth of about six feet, was named the zone of combustion. The author of this mapping out, as it were, the interior of the furnace, does not wish to be understood as confining its various functions within the respective spaces assigned to them; on the contrary, he admits the existence of considerable variations of position. My own observations, however, have led me to conclusions varying considerably from those adopted by Scheerer.

The fundamental cause of these differences seems to depend on the temperature considered as being required for a commencement of the reduction of the ore. By Scheerer the reducing zone is considered to require a temperature of 1000° to 1200° C. This change undoubtedly is not the same with all kinds of ores, but my experiments were conducted when using almost every variety of the mineral. According to the trials made a mixture of one volume of carbon dioxide and two volumes of carbonic oxide at a temperature of 410° removed 10 per cent only of the oxygen in Cleveland ore, and 37·8 per cent from an artificially prepared oxide. The composition of the gases at the different depths, however, indicates in an unmistakable manner the nature of the action which is going on at any particular point. A table has been prepared from actual analyses of the gases which gives the quantity of oxygen present for every 1000 parts of metal produced, and to this is added the weight of carbon they contained. The results vary, but the general inference to be drawn from the observations made on furnaces of eighty feet is that by the time the minerals have passed through a space of eight feet of the depth they have to travel all the oxygen susceptible of removal from the ore in the upper region is found in the gases, the remainder being retained until it reaches the zone of fusion. The same is the order of action in a somewhat modified form which was found to prevail in the case of furnaces 48 feet in height.

On casting the eye along the lines of figures a somewhat remarkable circumstance is apparent, viz., that the quantity of oxygen per 1000 of pig-iron gradually

decreases as the gases ascend until they approach the upper region, when it commences to increase. This had been the subject of observation for many years without any complete explanation being given of its cause. Dr. Percy, among others, bestowed some attention to the circumstance without arriving at any opinion satisfactory to himself. It is a little extraordinary, so far as I have seen, that no notice has ever been taken of the fact that the carbon in the gases followed the same law. While engaged in investigating the action of furnace gases on the ore, a peculiarity was observed previously unknown to me, viz., that large quantities of carbon were deposited by the dissociation of the reducing gas, the action being $2CO = CO_2 + C$. Experimentally I ascertained that spongy iron, as well as oxide of iron, was capable of producing the change, and that thirty per cent of carbon dioxide, mixed with the carbonic oxide, arrested the reaction, the temperature at the time being 420°. Dr. C. A. Wright, who subsequently became chief chemist of our laboratory, was asked to continue the examination. The conclusion arrived at was the impossibility of effecting the complete reduction of E_2O_3, or of any oxide, by CO. On the contrary, when metallic iron known to contain no oxygen was exposed to a current of this gas, carbon was deposited and oxygen absorbed. It would seem, therefore, that this absorption of oxygen by the iron and precipitation of carbon suffice to explain the disappearance of these two elements from the gases, and that they remain in this condition until the fusion of the iron, in contact with intensely heated carbon, liberates the oxygen as well as that portion of the carbon which is not absorbed by the metal in order to produce pig-iron.

So far, then, as the analyses given in Table III. enable us to judge, instead of the upper two-thirds of a furnace being required for the purposes of reduction, no material change is effected after passing through 18 feet in a modern furnace of 80 feet in height. After this the composition of the gases, and, therefore, of the minerals, remains pretty steady until the vicinity of the tuyères is reached, with the consequences already referred to.

Of the excess of oxygen at the zone of combustion it is highly probable that a portion is due to the reduction of P_2O_5, SiO_2, SO_3, and CaO. In the case of Cleveland iron I have estimated this at 54 parts per 1000 of pig-iron produced, but the average total oxygen beyond that furnished by the blast in the first two instances given was 130 parts. At this rate there must have been 76 parts of oxygen liberated from the oxide of iron, which is equal to 19 per cent of that originally combined with the iron in the ore.

It may be appropriate here to refer to what may be taken as a typical expression of the working of a blast furnace in respect to the presence of carbon dioxide. An analysis of the gases is therefore inserted, drawn from an 80-feet furnace at various levels, with the simple remark that it is improbable that carbon dioxide can exist for any length of time when exposed to incandescent coke at the temperature which prevails at the depths mentioned in the last two columns.

Something like forty years ago the escaping gases from the blast furnaces, rich as they were in carbonic oxide, were permitted to burn wastefully on the surface of the minerals charged at the throat. This meant a loss of about 54 per cent of the heating power of the coke. For reasons already given it was of course impossible to utilise much of this heat in the actual smelting of the ore, because of the necessity of preserving a large excess of carbonic oxide in the gases. This, however, constituted no reason why, apart from the furnace work itself, this vast quantity of gaseous fuel should not have been utilised, as it no doubt would earlier have been, had the ironmakers known, as they now do, its full value. To-day all the blast and other engines are driven and the air is heated at our blast furnaces by fuel formerly wasted, and this without any labour for stoking being required. In Great Britain alone the annual saving is fully equal to four million tons of coal.

In connection with the other volatile products which accompany the iron smelter's work I will only mention ammonia. Some qualities of coal admit of being used in the raw state. In this case, as in distilling coal for illuminating purposes, ammonia is generated and may be collected. Instead, however, of the ammoniacal vapour being all contained in the hydrocarbons, as in gas-making, it is diluted in addition with all the fixed carbon as oxides and all the nitrogen of the atmospheric air used in its combustion. Nevertheless, Messrs. Bairds, of the Gartsherrie works, and others, are manufacturing large quantities of ammonia sulphate from the ammonia so obtained. A similar object is achieved by attaching the necessary condensers to the apparatus for coking coal. The process of distillation is then carried on in hermetically closed ovens heated by the combustion of the gases evolved. These, before reaching the fire-place where they are burnt, are deprived of their ammoniacal vapours by passing through condensers provided for the purpose. Previous, however, to this being done, the waste heat from the coking process had been applied for generating steam, so that at certain collieries in the county of Durham all the mechanical power is obtained without any coal being specially burnt for this purpose.

Before speaking of the next and last great improvements in connection with my subject, I should like to say a few words, and a few words only, respecting steel, a well-known and most valuable compound of iron and carbon. Let me first observe that it seems improbable that this substance was not earlier known to the ancients, as was at one time supposed. The facility with which the metal combines with carbon renders it very unlikely that acieration would not occasionally take place when iron itself was the object of the manufacturer. Certain it is that Agricola, who wrote in 1556, describes in Latin a mode, apparently as well known as that of making iron itself, of making *Acie*. The engraving in his "De re Metallica" shows bars of malleable iron placed upright in a charcoal fire resembling that of a Catalan hearth. These, after an exposure of several hours to the incandescent charcoal and hot carbonic oxide, were found changed to steel and employed as such.

After the invention of the blast furnace pig-iron was placed in a similar hearth, and while in a melted state a blast of air was directed upon the molten metal, until just as much carbon remained with the iron as constituted steel. This mode of procedure continued to be practised long within my own recollection, and may, for what I know, still be followed in some districts. The subject of steel-making occupied the attention of Hassenfratz, of Réaumur, and others, but practically the only process followed until 1865 was the well-known one of cementation.

Since the days of Fourcroy it was ascertained that in addition to the iron carbon was an essential ingredient in cast metal, but invariably accompanied by more or less silicon, and whenever the minerals contained sulphur or phosphorus these metalloids were also present. The nature of the actions employed for ridding the product of the blast furnace of these substances so as to render it malleable had also been carefully examined and explained by the light of scientific investigation. The manufacturer had, it is true, learnt by experience and observation how to produce an article of excellence without much knowledge of the science of his art. Among other things he ascertained that to obtain a ton of wrought iron he required the heat of an equal weight of coal in the puddling furnace; but he did not know, nor did even men of science, I think, ever dream, that the oxidation of the metalloids in the pig-iron, and that of a small portion of the metal itself, would afford heat enough to enable the workman to dispense with the use of all coal in the process of conversion. When, therefore, the iron trade was informed in a paper read before the British Association in 1856, entitled "A Mode of Making Iron without the Use of Fuel," its author, Henry Bessemer, was set down by the

iron trade as a deluded enthusiast. At that period I doubt whether ten pounds of wrought iron had ever been seen in a state of fusion at one time. Bessemer, in his description, however, spoke of melting tons of it with no more heat than that afforded by the rapid oxidation of about 5 or 6 per cent of the weight of the pig-iron used. Not only, therefore, was the subject one of economic, but also of high scientific interest. Nevertheless, a mere statement of the title of the paper was all the notice bestowed by our predecessors in their *Transactions* on a discovery which has revolutionised the art of making iron. It is quite true that for some time it appeared as if the scientific aspect of the question were to constitute its only recommendation, for the malleable iron made in a Bessemer converter proved unmanageable when hot, and destitute of strength when cold. Finally, it was ascertained that phosphorus was the source of the evil, and, further, that while carbon and silicon could be almost entirely removed from the molten metal, this third metalloid remained unaffected by the treatment. The extent to which the hurtful influence of phosphorus makes itself felt in the wrought iron obtained by the Bessemer process is somewhat remarkable, because while two- to three-tenths per cent is often present in puddled bars of fair quality, probably no consumer would accept Bessemer steel when it contains half of this amount. The first success was obtained in Sweden, where, by using pig-iron containing a mere trace of the objectionable substance, a product was obtained which was satisfactory. For many years the beneficial effect produced by manganese on steel had been well known, and it occurred to R. F. Mushet, son of David Mushet, one of, if not the earliest scientific metallurgist in the United Kingdom, to try its influence in the converter on iron made from the hematite iron of the West of England, which contained from 0·05 to 0·1 per cent of phosphorus. This addition, apparently by its removing occluded or combined oxygen in the molten iron, afforded the necessary relief, and the operation being one of extreme simplicity, enables steel or wrought-iron to be produced at a greatly reduced cost. To such an extent has this been carried that ore is brought by sea over a distance of 1000 miles to Middlesborough, and from it steel rails are made more cheaply than a greatly inferior article of iron can be produced from the abundant and economically wrought bed of ironstone found within a couple of miles of that town. As an example of the facility of conversion may be adduced the fact that the molten metal is brought direct from the blast furnace, turned into steel or ingot iron as the case may be, and the heat evolved by the operation is sufficient to enable the product in many cases, without further use of fuel, to be taken direct to the mill and rolled into a finished bar.

We have just seen that 0·1 per cent or thereabouts of phosphorus renders steel or ingot iron valueless; in like manner very insignificant variations in the quantities of carbon or silicon materially affect their quality. Now the blow, as it is termed, in a Bessemer converter may be accomplished in from twelve to fifteen minutes. It is clear, therefore, the opportunity of ascertaining the precise quality of the steel is one of very short duration. It is, I think, not disputed that a product can be obtained by this process possessed of very high, if indeed not of the highest, excellence, but it is also pretended that the quality is not sufficiently uniform for certain purposes. The ordinary reverberatory furnace is incapable of affording the necessary temperature for melting steel or wrought-iron, but by employing the fuel in a gaseous state, and by heating the air and gas before they are brought together, as is done in the valuable furnace suggested by the Messrs. Siemens, the heat is so intensified that wrought-iron in it is rapidly fused. Steel is now largely made in such furnaces, either by mixing wrought and cast-iron, as proposed by M. Pierre Martin, or by means of cast-iron alone, when the carbon is removed by the addition of iron ore and some limestone, in which case, by the agency of the ore, the metalloids are oxidised and removed from the bath of iron. Some hours being required for this, sufficient opportunity is afforded for ascertaining the progress of the operation.

The cause of the iron in the Siemens furnace, as well as in the Bessemer converter, retaining its associated phosphorus in time began to attract the attention of chemists. In each case the expulsion of the metalloids is effected by oxidation. The carbon is gasified, and the silicium, on being acidified, is absorbed, and forms a slag containing usually 45 to 50 per cent of silicic acid. In the presence of such an excess of this substance any phosphoric acid, if formed, could not be absorbed by the slag. It was the late M. Grüner, of Paris, who, in 1867, first pointed out this fact, and he it was who first recommended the use of lime in order to render the slag basic instead of acid. Further, in order to avoid the presence of silica, he recommended at the same time that the converter should be lined with lime instead of with fireclay.

The same subject engaged my own attention, when guided by the fact that, as oxide of iron in the puddling furnace was capable of acidifying and removing a large quantity of the phosphorus as iron phosphate, it might be possible, by keeping the temperature of the metal below that required for the process of puddling, to make this removal more complete. The result of these experiments was communicated to the Iron and Steel Institute in March, 1877, when it was shown that pig-iron containing 1·75 per cent of P could, in a few minutes, have this reduced to 0·2 per cent. This process is now being used in the United States for freeing cast-iron from its associated phosphorus.

The rapid destruction of the ordinary Bessemer converter led Mr. G. I. Snelus to consider the practicability of using a lime lining, and on experimenting with this on a working scale he confirmed the opinions previously enunciated by Grüner by observing that the presence of lime had removed a considerable quantity of the phosphorus. These discoveries constitute the foundation of the very important basic process of Messrs. Thomas and Gilchrist, which consists in adding lime to the molten steel in a converter constructed on the principle described by Mr. Snelus. Considerable difficulty had, however, been experienced by this metallurgist in the attachment of the lime lining to the walls of the converter. This important question was solved by Mr. Edw. Riley by exposing dolomite to a very high temperature in order to prevent further shrinking, and then grinding and mixing the powder with coal-tar. This formed a species of cement, which is applied to the sides and bottom of the converter in the form of bricks or as cement. Doubtless, simple as the idea is, it has greatly contributed to the success of the basic process.

The acidification and subsequent transference to the slag of the phosphorus by the basic treatment has led to its application to agriculture. For this purpose the slag is ground to a fine powder and sprinkled over the land without any further preparation. By this operation an indispensable element of animal life is derived from the remains of living creatures which, ages ago, found a grave in the ferruginous mud destined to become the great Cleveland bed of ironstone.

Before closing this portion of my official duty I cannot refrain from tendering to chemists an assurance of the great advantage the manufacturers of iron feel they have derived from the lessons taught them by chemical science. I am the more anxious to do this because we, among others, have been reminded that we are losing the supremacy among industrial nations we once enjoyed for want of that knowledge of chemistry which is more assiduously cultivated abroad than it is in our own country. I am not prepared to deny that the opportunities for acquiring a scientific education are less generally spread here than is the case in France, Germany, or Belgium; but for this the nation, and not the iron trade in particular, is responsible. It must also be ad-

mitted that as manufacturers we no longer stand so far above other lands as we formerly did. In this result any differences of education are in no way concerned, for if I were to classify the nationalities of the various inventions enumerated in the course of my remarks the fears of those who are alarmed at the appearance of a Belgian girder or a German steam-engine on our shores would, I think, be allayed. Perhaps I might be allowed to offer a very few words on the technical side of this important question of education. Much I shall not be able to say, because I have not yet been able to learn the precise position the subject occupies in the minds of its most earnest advocates. If it means, as is sometimes alleged, a system by which, along with scientific instruction, manual dexterity in the use of tools or a practical knowledge of various manufacturing processes has to be acquired, I confess I am not sanguine as to the results. Certain I am that if foreign workmen are more skilful in their trades, which, as a rule, I doubt, and which in the iron trade I deny, this superiority is not due to scientific training in the manner proposed, for in this they possess, so far as I have seen, no advantage over our own workmen. My objection to the whole system is the impossibility of anything approaching a general application being practicable. I have not a word to say against the rudiments of science being taught wherever this is possible. The knowledge so obtained may often give the future workman a more intelligent interest in his employment than he at present possesses, but I think they who expect much good to attend such a thin veneer of chemistry or physics do not take sufficient account of the extent of the knowledge already possessed by more highly educated men who are now directing the great workshops of the world. It is by extending and enlarging this that substantial aid has to be afforded to industry and science, and not by teaching a mere smattering in our primary or any other schools. In the case of young people who, from necessity, must leave the schoolroom at an early age, my own leaning is towards the present system, with the addition of drawing and some natural science. By it certain important lessons are taught, which, if not followed under the discipline of the schoolmaster, run some risk of being entirely neglected. After this, probably, the playground will be found more useful and much more popular with schoolboys than trying to learn a trade by means of tools which, before he has to use them in earnest, may be thrown into the scrap heap.

As a national question, the attention of the Government, Imperial or municipal, ought to be directed to the importance of establishing in all great manufacturing centres institutions resembling that of the Physical College of this city. These should consists of appropriate and even handsome buildings, properly furnished with all the instruments and appliances required for teaching the sciences in their practical bearings on industrial pursuits. In Newcastle, as well as in other places, this has been done on a fairly ample scale, and the advantages the College of Science in this city are capable of affording are offered on such terms that no one can plead expense being a barrier to mental improvement.

Bearing in mind the importance of the subject, and remembering, as my colleagues and myself do, the difficulties we have had to encounter and those we have still before us, I am strongly of opinion that the erection and maintenance of colleges of science should not be left to the accidental liberality of the few, but should be taken in hand by the nation at large.

The Passivity of Cobalt.—Ernest Saint-Edme.—The so-called *passive state* of iron and of nickel is merely a chemical property possessed by their nitrides. This state of passivity is connected with the degree of affinity of the metal for nitrogen, *i.e.*, in a decreasing order for iron, nickel, and cobalt.—*Comptes Rendus*, Vol. cix,. No. 8.

THE "AMINES" SEWAGE PROCESS.

On September 18 we had the pleasure, in company with a very numerous gathering of experts, journalists, and municipal officials, of witnessing the working of this new process at the Wimbledon Sewage Works. The idea of using crude trimethylamine—in other words herring-pickle—for the treatment of sewage seems to have been first entertained by Samuel Walter, who obtained an English patent, No. 5283 of A.D. 1882, in which he claims "adding herring-brine or *sea-salt* to sewage or other foul waters"; and in the body of his specification he mentions that such herring-brine or salt is to be diluted with lime-water.

On October 24th, 1888, Herr H. Wollheim obtained a patent (No. 15,321) in which he proposes to treat the sewage with milk of lime to which trimethylamine or an isomer has been previously added. This inventor seems to have a more distinct aim in view than S. Walter, who possibly uses herring-brine merely as a cheap waste form of common salt. Herr Wollheim, on the contrary, evidently recognises the trimethylamine present in the herring-brine as the active ingredient.

The process which we witnessed was as follows:—Milk of lime was mixed in the proportion of about 4½ lbs. per 1000 gallons, along with about 18 ozs. of trimethylamine. It does not sufficiently appear whether these 18 ozs. are to be actual trimethylamine, or brine, &c., in which such a quantity of trimethylamine has been found to be present.

On the addition of this mixture to the sewage precipitation was rapid. Samples of the effluent dipped up for inspection were fairly inodorous and colourless. They were, however, strongly alkaline, as were also the deposit or sludge and its drainings.

Occasionally, in walking about the works, we encountered a disagreeable smell, not excrementitious nor briny, but rather fishy, such as is commonly experienced where sewage is treated by any alkaline process. We are not, however, free to lay this odour to the charge of the "Amines" process, since in a closely adjoining set of tanks the ordinary Wimbledon treatment was at work "for the sake of comparison,"—a most unfortunate arrangement. Some sludge which had been laid out in a tank ever since August 23rd was submitted to examination. In colour and texture it was very like a lime deposit, but it was without the disagreeable smell which such sludges always have.

Such are the points which were to be seen, and which were shown, without any reservation. In a circular which was distributed, and in an address delivered by Mr. Ellice-Clark, C.E., the Engineer to the "Amines" Syndicate, we were informed that by this treatment the sewage was completely disinfected and "sterilised," all microbia being entirely destroyed. This result, which is vouched for by Dr. Klein, is extremely interesting. This eminent bacteriologist found 2,400,000 organisms per c.c. in a sample of sewage, whilst in some of the same sewage, after treatment by the "Amines" process, there remained none at all. This is the more curious as Mr. A. Winter Blyth, M.R.C.S., in a paper entitled "A Study of Disinfectants by New Methods," communicated to the Royal Society in 1886, found that the amines had but feeble disinfecting powers. Here there is evidently need of further research.

We were also told that the effluent from the "Amines" process underwent no secondary fermentation — an important point on which nothing could be ascertained during a few hours' inspection. If this is the case in an alkaline liquid, *i.e.*, under circumstances most favourable for the production of microbia, the disinfecting powers of trimethylamine must be strong and persistent beyond comparison.

It is to be regretted that in the circular distributed among the visitors no chemical analysis was given either of the effluent or of the dry deposit. This is an important

omission, since a water, though absolutely sterilised, may be utterly unfit either for domestic or industrial purposes. For the waste waters of manufactories, disinfection is, indeed, a very secondary matter.

Some of the advantages attributed, however truthfully, to this process are shared by other methods of sewage treatment. Thus the removal of suspended matters, organic or inorganic, is very generally effected. We were told that fish can live in the effluent from the "Amines" process if previously diluted with ten vols. of river water. But we have seen fish living for months in an undiluted effluent. The "necessity for hurried disposal of wet sludges at any cost" exists only in cases of lime processes, and is not common to sludges obtained by neutral or acid processes, which are not an "intolerable nuisance," and which,—it would be invidious to mention names—so far from "begging for customers," find a ready sale at good prices.

The weakest point of the "Amines" process is the lime-character of its manure. No sensible farmer or gardener applies lime to his land in conjunction with farm-yard manure, night soil, ammonium salts, or other nitrogenous matter, as, in the long run, even calcium carbonate expels the nitrogen in the form of ammonia.

The strongest point of the "Amines" process is its economy. The lime process has been able to maintain its ground in virtue of its being cheap—and nasty; and if this new invention does away with the nastiness without sensibly affecting the cheapness it has doubtless before it no small future.

We learn that the Wollheim Syndicate has bought up or leased the patent-rights of S. Walter.

A QUICK METHOD OF PREPARING SILICON, ALUMINIUM, AND OTHER CHLORIDES IN QUANTITY.

By H. N. WARREN, Research Analyst.

The usual method resorted to for the preparation of anhydrous chlorides of those elements which are not themselves usually available, but obtainable rather as oxides is, as is well known, based upon the thorough mixing o the same with a sufficiency of carbon to replace the oxygen present, enclosing the same in a suitable enclosure consisting of either clay, or, more generally, glass combustion tubing, raising the same to an elevated temperature, and exposing the same to the action of chlorine gas. This, however, has, as regards a process, considerable drawbacks, both on account of the bulk of the mixture and the high temperature that is frequently required before decomposition of the oxide is effected.

For the preparation of silicon chloride, a sample of silicon-eisen containing about 15 per cent silicon was selected, introduced into a deep clay retort provided with a tubulure, and connected with an apparatus evolving dry chlorine gas, the pipe conveying the gas passing nearly to the bottom of the retort, while the stem of the same was connected to a suitable adapter, maintained at the required heat by the aid of hot water, and intended to condense or retain the volatile ferric chloride which would naturally accompany the silicon chloride, the end, or termination of the adapter being further connected with a suitable refrigerator containing a mixture of salt and ice in order to collect the volatile tetrachloride of silicon, $SiCl_4$.

The retort and its contents being now raised to redness by the aid of ignited charcoal, and the chlorine thus allowed to play into the same, almost immediately the dense greenish yellow vapour of gaseous ferric chloride is observed traversing the space within the adapter, and speedily condensing into the form of brilliant plates upon the walls of the same, while, at the more remote end, is observed the condensation of the silicon chloride, not unfrequently contaminated by the presence of small quantities of ferric chloride, which may, however, be entirely removed by subjecting the latter to distillation.

Further advantages may be obtained by substituting for the chlorine gaseous hydric chloride. This gas, on account of its forming with the iron a ferrous salt practically non-volatile at ordinary temperatures, is itself retained in the retort, and, at the termination of the reaction, may be detached by pouring the same while in the liquid form, while, at the same time, a further charge may be introduced. Thus, by acting upon the element silicon at an elevated temperature by means of gaseous hydric chloride a still more volatile liquid chloride of silicon is obtainable, corresponding to a hydro-trichloride, and represented by the formula of $SiHCl_3$. In this instance, however, the formation of silicon itself, which in the elementary form is by no means easy as regards its preparation, is absolutely necessary; but, by substituting for the same a sample of silicon-eisen containing a rich percentage of silicon, the corresponding chloride may be as readily prepared as in the former instance.

For the preparation of aluminium chloride an alloy of iron and aluminium containing about 10 per cent of the latter was selected, and the chloride thus obtained purified by intimately mixing it with iron borings and distilling the same; or the pulverised regulus mixed with common salt previous to exposing it to the action of chlorine yields, as a sublimate, aluminium-sodium-chloride.

Silicon chlorides, as also the corresponding bromides and iodides, which may be formed by a process analogous—namely, the substitution of either bromine or iodine in place of chlorine—are, at present, of no commercial value, but a simpler process than that usually resorted to may possibly be of benefit to those requiring the same when pursuing organic research. Their complete volatilisation have also induced the performance of several experiments with a view of ascertaining whether the reaction obtained is attended with any practical value.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

NOTICES OF BOOKS.

Appendices to the Investigation on Capillary Analysis and its Various Applications, as also on the Ascent of Colours in Plants. ("Beilagen ueber Capillaranalyse und ihre verschiedenen Anwendungen sowie ueber das emporsteigen der Farbstoffe in den Pflanzen"). Reprinted from the *Transactions of the Imperial and Royal Technical Museum of Vienna*, New Series, vol., ii., 1888, Nos. 3 and 4, and vol. iii., Nos. 1, 2, 3, and 4. By Prof. Dr. F. Goppelsroeder. Mulhouse: Wenz and Peters.

These appendices are concerned, in the first place, with the demonstration of the several colouring-matters in the organs of plants by means of capillary analysis. Plants belonging to sixty-seven families have been carefully examined, in most cases in their roots, stems, leaves, buds, and flowers.

In a second series of experiments the material operated upon was the alcoholic extract of the roots of plants prepared in the complete absence of sunlight.

A third series is devoted to an examination of the changes which the alcoholic extracts of the different organs of plants undergo on the addition of ammonia, caustic potassa, hydrochloric and sulphuric acids.

An appendix to Chapter II. gives an account of Schœnbein's original experiments on separations effected by means of capillary attraction.

A further appendix gives a reproduction of a memoir by Dr. F. F. Runge, which appeared as early as 1855, and

bears the title, "The Formative Impulse of Substances represented in Autogenous Pictures." Runge's original treatise is rare, if procurable; the abridgment here given will be interesting to all who wish to comprehend the possible effects of capillarity.

The Industry of Colours ("Die Farben Industrie"): A Quarterly Report on Results in the Region of Coal-tar, in the Chemistry of the Aromatic Compounds, of Artificial Colours, of Dyeing, Bleaching, Tissue Printing and Finishing. By E. Börnstein. Part 1st, October—December, 1888. Berlin: Mayer and Müller.

This new quarterly journal is a proof of the growing importance of that department of chemistry which concerns itself with the production and the application of colouring-matters. Various journals, English, French, and German, which devote themselves to subjects of this kind have certainly not been wanting, but the "Report" now before us possesses the advantage of presenting a complete view of all that has been done in this department during the past three months. To the many chemists and industrialists who have not time to search through an extensive series of journals and transactions this "Report" will prove a great convenience.

The arrangement here adopted is the following:—Coal-tar; the aromatic compounds, viewed in general, physically, physiologically, and theoretically; the benzol- and diphenyl-groups; the phenilised fatty hydrocarbons; the indol-, quinoline-, naphthaline-, phenanthene-, and anthracene-groups.

The third section treats of mordants and colours, and the fourth of bleaching, dyeing, printing, and finishing.

Chromelectro-Chemical Communications ("Farbelectrochemische Mittheilungen"). By Prof. Dr. Friedrich Goppelsrœder. Mulhouse: Wenz and Peters.

The author of this interesting pamphlet has been for some years engaged with the task of generating colouring-matters by the electrolysis of neutral, acid, or alkaline solutions of various salts of aniline, of the toluidines and their homologues, and also of the naphthylamine salts, phenol, &c. Not merely has he obtained in this matter colouring-matters, *e.g.*, alizarin, but he has succeeded in their electro-chemical fixation upon tissues. Specimens of this novel and interesting development of tissue-printing were exhibited by the author at the Manchester Jubilee Exhibition, in 1887. Thus, designs in aniline-black have been produced upon white, turkey-red, and vat-blue cotton-cloth, as also upon paper and parchment-paper.

One pattern shows the conversion of turkey-red into alizarin orange by the electrolysis of a solution of potassium nitrate. In another there is a white discharge on turkey-red produced by the electrolysis of ammonium chloride.

Many of the curious results here described cannot be made intelligible without reproductions of the accompanying illustrations. It seems to us, however, that Dr. Goppelsrœder's process, or rather processes, carry in them the germs of much that is likely to be of no small value—perhaps of a reorganisation of no small portion of the tinctorial arts. The author says, indeed, "The future must solve the question whether cylinders or plates acting as electrodes, plane or engraved, can find practical application, whether for the production of self-coloured grounds, or for the production of white or coloured designs upon coloured or white ground, discharges upon vat-blues, turkey-reds, &c., or other electro-chemical effects. The idea, however, of seeing a colour produced and in the same moment fixed upon the fibre has something supremely attractive for every chemist who appreciates Prof. Goppelsrœder's motto: "*Scientia vivat, crescat, floreat.*" Hence we can only hope that no unforseen economical difficulty may interfere.

On Capillary Analysis and its various Applications, as well as on the Ascent of Colouring Matters in Plants. By Professor Dr. Friedrich Goppelsrœder. Vienna: The author.

Capillary analysis is a method for the detection and separation of colouring-matters occurring in mixtures, by means of the varying speed with which they ascend in capillary tubes, *e.g.*, in unsized paper. The idea of utilising this phenomenon in the analysis of colouring-matters seems first to have occurred to the late Prof. Schœnbein, of Bâle, in or about 1861, and to have been elaborated by the author, who had been Schœnbein's pupil.

The method employed was substantially this:—Slips of pure filter-paper were suspended so as to dip for a few m.m. into the watery, alcoholic, ethereal, or other solutions of colouring matters. On withdrawal it was observed that if more than one colour was present they appeared in a series of successive strata. In this manner the impure coal-tar colours which were first introduced into commerce were easily resolved, qualitatively at least, into their constituents.

A similar method, depending likewise on capillary attraction, was described in an English work in 1870 (Slater, "Manual of Colours and Dye-wares"). The author states in his second edition that he "had used it privately, and shown it to friends since about 1860." But, however this may be, it is evident that the Schœnbein-Goppelsrœder method of applying the test is much more convenient than that of Slater, who merely placed a drop of the solution upon a piece of filter-paper, and observed whether the spot produced was homogeneous in colour, or spread out into zones of different colours. Goppelsrœder, after withdrawing his slips of paper from the solution, lets them dry, cuts off the parts which display different colours, dissolves each of them out by means of suitable solvent, and, if necessary, submits each solution separately to capillary analysis until perfectly pure colours are obtained.

Dr. Goppelsrœder next describes the application of capillary analysis in the detection of organic substances. In some cases minute traces may be detected in this manner.

In a following section we find this method applied in organic, and especially in tinctorial chemistry. The author points out that in recent coal-tar colours the traces of foreign matters are exceedingly slight in comparison with those observed a few years back.

Dr. Gopplesrœder considers that as far as colouring-matters are concerned, the capillary method is an excellent complement to absorption spectroscopy.

Capillary analysis, the author holds, will also prove of great importance in hygienic and forensic chemistry, in the detection of adulterated wines and beers, and pathological analysis.

This treatise, in short, must be recommended to almost every class of chemist. There are, we believe, few who will not find here useful hints, perhaps clues to new spheres of research.

CORRESPONDENCE.

THE TITRATION OF FERRIC SALTS.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lx., p. 93), which has only just come under my notice, Mr. Clemens Jones contributes a paper on the titration of ferric salt solutions, in which the following sentences occur:—

"D. J. Carnegie (Chem. News, lvii., No. 1481) says that ferric solutions are instantaneously reduced by the use of zinc-dust. But there are obvious objections to its employment in quantitative work."

The obvious objections are not, however, stated.

If Mr. Clemens Jones had referred to the Chemical Society's *Journal* (*Trans.*, 1888), where my paper appeared *in extenso*, he would have found that the quantitative method described in connection with the reduction by zinc-dust gives very good results indeed, being in fact practically identical in principle with the one he himself advocates, viz., momentary contact of *slightly* acidified ferric salt solutions with finely divided zinc, followed by filtration from the excess of zinc prior to titration. As regards the filtration, the two methods differ, but the reversed filtration which I suggested is very simple and, I feel convinced, quite as effective as the method described by Mr. Clemens Jones, which involves such large and costly apparatus.

Zinc-dust is much more readily obtainable than pulverised zinc, and is generally so free from reducing impurity that the amounts employed in ordinary titrations do not introduce appreciable errors.—I am, &c.,

DOUGLAS J. CARNEGIE.

Gonville and Caius College, Cambridge.

VERMILION OR VERMILLION.

To the Editor of the Chemical News.

SIR,—The correct spelling is undoubtedly "vermilion." The word is so given in Ogilvie's "Imperial Dictionary," 1883; also in Buchanan's "Dictionary of Science and Technical Terms," 1876. I have no other works of general reference easily accessible, but the first-named dictionary should be sufficient authority. The Italian *vermiglio*, and French *vermeil*, from the Latin *vermiculus*, are equivalents.—I am, &c.,

EDWY GODWIN CLAYTON.

Chemical Laboratory,
43 and 44, Holborn Viaduct, E.C.,
September 11, 1889.

VERMILION OR VERMILLION.

To the Editor of the Chemical News.

SIR,—The French equivalent for ver-mil-ion is vermillon, and we have substituted an *i* for an *l* to produce something akin to the *y* sound of the double French *l*. If we use two *l*'s we spoil this effect, thus: ver-mil-lion. There appears, therefore, to be no doubt but that the correct way to spell vermilion is with one *l*. In those cases where two *l*'s are used they may be looked upon as slips of the pen caused by our familiarity with *million*. Mr. White is not very happy in his reasoning, that it should be spelt with one *l* because *vermeil* has only one; what about the feminine, *vermeille*? Besides, we might just as well argue that the correct way to spell battle is "batlle," because it is derived from or allied to *bataille*.—I am, &c.,

J. G. MCINTOSH,
Lecturer on Oils, Colours, and Varnishes,
Polytechnic Institute.

Service Chemistry. — An important volume, freely illustrated, entitled "Service Chemistry," will be issued immediately by Messrs. W. B. Whittingham and Co. It is a work upon which Professor Vivian B. Lewes, Lecturer at the Royal Naval College, has been laboriously engaged for the past year, with a view to bringing the entire subject up to the latest date. Chemistry, as affecting not only the Navy and the Army, but also the Merchant Service, is treated with technical detail.

The Use of Water-Gas.— MM. J. Lunge, O. Wyss, and M. Rothenbach (*Zeits. Angew. Chemie*).—The high proportion in water-gas of carbon monoxide necessitates special precautions. In the state of Massachusetts a lighting-gas may not contain at the outside more than 10 per cent carbon monoxide. For communicating to water-gas such an odour that an escape may be at once recognised the authors propose the addition of mercaptan. Further experiments are needed to decide whether this odour may not be lost in traversing the mains.

SCHOOLS OF CHEMISTRY.

THE following information was received too late for insertion in our Students' Number:—

GLASGOW AND WEST OF SCOTLAND TECHNICAL COLLEGE.

The Courses of Lectures, &c., are given in the various Buildings as follow:—

ANDERSONIAN BUILDINGS, 204, GEORGE STREET.

Professor of Chemistry.—William Dittmar, LL.D., F.R.SS. Lond. and Edin.

Chief Assistants.—James Robson and William Cullen.

Two Courses of Experimental Lectures on Chemistry: Daily from 10 to 11.—Junior, on Tuesdays and Thursdays; Senior, on Mondays, Wednesdays, and Fridays. The Lectures up to the end of the year are devoted to an Elementary Exposition of the Philosophy and the Methods of the Science, as illustrated by the History of the Non-metallic Elements. The rest of the Session is divided between the Chemistry of the Metals and Organic Chemistry, select chapters. In addition to occasional extemporised examinations during class hours, five written examinations are held during the Session, on Saturdays from 10 to 12. Fee, £2 2s.

The Laboratory is open daily (Saturdays excepted) from 10 to 4. Advanced students may obtain permission to work privately on Saturdays also until 1 p.m. The teaching is conducted on the tutorial system, each student working by himself, at a separate place, and on his own subject. Hence students of any grade of advancement may enter at any time, and the course of instruction can be adapted to the special requirements of the individual. Original research is not forgotten, but the Professor makes it a strict rule not to use his students as his private assistants in connection with his own investigations, and rather to discourage original research with students who have not yet obtained a sufficient mastery of all the practically important methods of chemical analysis and of preparative chemistry. Fee per month, £2 2s.; due in advance. For any period of six months or more, if paid in advance, at the rate of £1 15s. per month. The fees include the use of all the ordinary reagents, and of the resources of the laboratory generally; but the student has to find his own small apparatus (test-tubes, beakers, &c.), and also a few of the more expensive reagents—*e.g.*, chloride of platinum, nitrate of silver, molybdate of ammonia.

Supplementary Courses of Lectures and Laboratory Instruction are also given by the Assistants under the superintendence of the Professor.

An Evening Course of Lectures on the Fermentation Industries will be delivered by the Professor on Fridays from 8 to 9 o'clock, commencing on 18th October.

THE "YOUNG" CHAIR OF TECHNICAL CHEMISTRY, YOUNG LABORATORY BUILDINGS, 60, JOHN STREET.

Professor.—Edmund J. Mills, D.Sc. (Lond.), F.R.S.

Assistant.—Mr. William Baird.

This Chair has for its object the instruction of Students in Chemistry as applied to the various branches of industry in Chemical and other works.

LECTURES.—I. *Principal Course.*—A Course of Twenty-four Lectures will be delivered on Mondays, at 3 p.m., commencing on October 7th. These Lectures will refer mainly to the application of higher Chemistry, and are more especially intended for manufacturers, inventors, chemical engineers, and senior chemical students. Fee for the Course, One Guinea.

II. *Chemical Engineering.*—A Course of Twenty-four Lectures will be delivered on Tuesdays, at 3 p.m., commencing on October 8th. These will deal mainly with the construction and use of chemical plant.

III. *Technical Organic Chemistry*—A Course of Twenty-one Lectures will be delivered on Wednesdays at 2.30 p.m.,

commencing on October 9th. This Course is more particularly intended for Dyers, Colour Manufacturers, Brewers and Distillers, Tar Rectifiers, Drysalters, and others interested in a knowledge of Technical *Organic* Chemistry. Fee for the Course, £1 1s.

Evening Courses.—There will be a special evening course of twenty-four lectures on Photography, commencing on October 1st. These Lectures will be illustrated, and will be mainly of a practical character.

Laboratories.—The Laboratories are open daily from 10 to 4, and on Saturday from 10 to 1 o'clock for practical working by the Students, under the superintendence of the Professor and his Assistants.

The Fee for attending the Laboratories is £20 per Session of Nine Months, £14 10s. for Six Months, £7 10s. for Three Months, or £2 10s. per month.

Photographic Department.—The Laboratory contains a dark room provided with suitable appliances for copying, enlarging, and reducing, as well as for field work. Provision will be made to place at the disposal of Students a course of instruction in Photography sufficient to qualify them for Engineering, Calico-printing, and other works. Fee, the same as for Laboratory work.

Inventors, Patentees, and others whose investigations require isolation and privacy, as well as professional advice, can have Private Laboratories placed at their disposal. Electric Cable has been laid to these laboratories for the supply, if required, of adequate power.

Agricultural Chemistry.—Mr. C. M. Aikman, M.A., B.Sc., &c., will give courses of Evening Lectures on this subject. Elementary, Tuesdays, at 7. Senior, Fridays, 7 to 9.

Further information may be obtained of the Professor, at the Young Laboratory, 60, John St., Glasgow.

SCIENCE AND ART BUILDINGS, 38, BATH STREET.

Metallurgy and Mineralogy.—Professor, A. Humboldt Sexton, F.R.S.E., &c. Assistants: J. Morrow Campbell, B.Sc., and R. Law.

A course of lectures on Metallurgy on Mondays, Wednesdays, and Fridays, at 4 p.m., commencing on 7th October. Section I. on Mondays: Fuel and Refractory Materials. Section II. on Tuesdays: Manufacture of Iron and Steel. Section III.; Metallurgy of the Useful Metals other than Iron and Steel. Fee for any Section, £1 1s.; for the complete Course, £2 2s.

A Course of Lectures on Electro-Metallurgy will also be delivered on Wednesdays at 5.5 p.m. Fee, £1 1s.

The Metallurgical Laboratory is open daily from 10 to 4. Instruction is given in all branches of practical Metallurgy and Assaying. Fee, £2 2s. a month or £10 10s. for the session.

A course of instruction in Mineralogy, including the use of the blowpipe, &c., is given on Tuesdays and Thursdays from 4 to 5. Fee, £1 1s. Practical Course on Tuesdays from 2 to 4. Fee, £1 1s.

Evening classes in Chemistry, Metallurgy, and Mineralogy commence on Monday, September 30th.

ROYAL COLLEGE OF SCIENCE FOR IRELAND.

Professor.—W. N. Hartley, F.R.S., F.R.S.E., &c.

Assistant.—T. A. Shegog, F.C.S., F.I.C.

The instruction in chemical science embraces:—General Chemistry—A course of 60 experimental lectures on mineral and organic chemistry. About 15 tutorial classes are held by the Assistant Chemist. Applied Chemistry—(*a*) A course of 30 lectures on chemical manufactures; (*b*) A course of 30 lectures on metallurgy. Analytical Chemistry—A laboratory course of practical work, including qualitative analysis, quantitative analysis, assaying, and instruction in chemical research.

The college supplies, as far as practicable, a complete course of instruction in science applicable to the industrial arts, especially those which may be classed broadly under the heads of Mining, Engineering, and Manufactures, and is intended also to aid in the instruction of teachers for the local Schools of Science.

The Faculty of Manufactures was originally termed the Faculty of Chemistry, and the diploma of this Faculty is recognised by the Council of the Institute of Chemistry. By the kindness of manufacturers in Dublin the Professor has been able to conduct students of this Faculty through the chemical works of the district.

Students may also enter for the separate courses and receive certificates after examination. Certificates of attendance are granted to medical and other students, and such certificates are accepted by the Royal University of Ireland.

Further particulars may be obtained from the Secretary, Royal College of Science for Ireland, Stephen's Green, Dublin.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 8, August 19, 1889.

Remarks on the Conditions in which the Fixation of Nitrogen is Effected by Clayey Soils.—M. Berthelot.—The author states that since he reopened the question of the fixation of atmospheric nitrogen a number of eminent experimentalists have obtained results similar to his own. The new doctrine of the fixation of nitrogen by the joint action of the soil and of living organisms may be considered as established.

New Researches on the Fixation of Nitrogen by Vegetable Mould. The Influence of Electricity.—M. Berthelot.—The gain of nitrogen effected under the influence of vegetation has always been greater with electrised tree-pots than with such as were not electrised, both under glass bells and in the open air, in spite of the inferiority caused by the inequality of illumination. The same conclusion was arrived at in experiments performed on bare soil, provided, indeed, with microbia, but free from any higher vegetation. These results taken collectively seem to render probable an especial action of electricity, which promotes the fixation of nitrogen both in the soil and in the course of vegetation.

On Phosphotungstic Acids.—E. Péchard.—The author has obtained four distinct acids containing, to 1 equiv. of phosphoric acid, 6, 5, 4, and 3 equivs. of metatungstic acid.

Chemical and Thermic Study of the Phenolsulphuric Acids. Orthophenolsulphuric Acid.—J. Allain-le-Canu.—This is essentially a thermo-chemical paper, and as such it does not admit of useful abstraction.

The Combustion-Heat of Certain Organic Compounds.—S. Ossipoff.—The substances experimented upon are teraconic acid, maleic anhydride, methyl fumarate, and methyl maleate.

MISCELLANEOUS.

British Association for the Advancement of Science.—The following are the names of the Officers and Committee of Section B (Chemical Science) of the Newcastle-upon-Tyne Meeting of the British Association:—

President.—Sir I. Lowthian Bell, Bart., D.C.L., F.R.S., F.C.S.

Vice-Presidents.—Sir F. A. Abel, D.C.L., F.R.S.; Professor P. P. Bedson, D.Sc.; J. H. Gladstone, Ph.D., F.R.S.; Professor F. R. Japp, M.A., LL.D., F.R.S.; Professor G. D. Liveing, M.A., F.R.S.; Professor H.

M'Leod, F.R.S.; Professor J. Emerson Reynolds, M.A., F.R.S.; W. J. Russell, Ph.D., F.R.S.; Dr. E. Schunck, F.R.S.; Professor W. A. Tilden, D.Sc., F.R.S.

Secretaries.—H. Forster Morley, M.A., D.Sc. (Recorder); D. H. Nagel, M.A.; W. W. J. Nicol, M.A., D.Sc.; H. L. Pattinson, Jun.

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The Papers brought before the Section were as follows:—

President's Address.

Report of the Committee on the Influence of Silicon on the Properties of Steel.

Report of the Committee on the best Method of Establishing an International Standard for the Analysis of Iron and Steel.

Professor Liveing.—On Eikonogen, a new Photographic Developer.

J. W. Hogg.—The Volatilisation of Lead Oxide and its Action on Glass, at Low Temperatures.

C. T. Heycock, M.A., and F. H. Neville, M.A.—On the Molecular Weight of Metals: an application of Raoult's Method to Alloys.

Dr. J. B. Readman.—The Manufacture of Prussiate of Potash.

Report of the Committee for the purpose of Inquiring into and Reporting on the present Methods adopted for Teaching Chemistry.

Prof. P. P. Bedson, D.Sc.—On the Manufacture of Aluminium from Cryolite.

J. Pattinson and Dr. H. S. Pattinson.—On Chilian Manganese Ore.

Professor Frank Clowes, D.Sc.—On Barium Sulphate Deposits from the Waters of Durham Coal-mines and in Nottingham Sandstone.

J. H. J. Dagger, F.I.C.—The Manufacture of the Alloys of Aluminium in the Electric Furnace.

Report of the Committee on the Bibliography of Solution.

Report of the Committee on the Properties of Solutions.

Report of the Committee on the Absorption Spectra of Pure Compounds.

Report of the Commit.ee on the Action of Light on the Hydracids.

Report of the Committee on the Silent Discharge in Oxygen.

Report of the Committee on the Bibliography of Spectroscopy.

Dr. Arthur Richardson.—A new form of Self-registering Actinometer.

Professor H. B. Dixon, F.R.S.—Explosion of a Mixture of Hydrogen, Chlorine, and Oxygen.

Professor H. B. Dixon, F.R.S., and J. A. Harker.—On the action of Light on dry Hydrogen and Chlorine.

Dr. A. P. Laurie.—On Artists' Colours.

Dr. William Newton.—Specific and Latent Heats in Relation to the Combining Heats of the Elements.

Dr. A. Scott.—Composition of Water by Volume.

P. Braham.—A Spectroscope without a Lens.

Discussion on Blast Furnace Practice.

Report of the Committee on Isomeric Naphthalene Derivatives.

Report of the Committee on the Formation of a Uniform System of Recording the Results of Water Analysis.

Professor Percy F. Frankland, Grace C. Frankland, and J. J. Fox.—Contributions to the Study of Pure Fermentation.

S. A. Sworn, B.A.—The Constitution of the Aromatic Nucleus.

S. A Sworn, B.A.—The Reaction of Benzoquinone with Potassium Cyanide.

J. B. Hannay.—A new White Lead.

Dr. Issac Ashe.—Dimidium: an attempt to Represent the Chemical Elements by Physical Forms.

P. J. Hartog, B.Sc.—Researches on Sulphites.

Dr. J. B. Cohen.—Metallic Aluminium as a Chemical Reagent.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Cement.—Can any reader refer me to papers on Portland cement, particularly those dealing with the chemistry of the subject, published here or on the Continent? I have Le Chatelier's work.—Cement.

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THE CHEMICAL NEWS.

Vol. LX. No. 1558.

ON EIKONOGEN, A NEW PHOTOGRAPHIC DEVELOPER.*

By Professor G. D. LIVEING, F.R.S.

This substance is the sodium salt of amido-β-naphthol-β-sulphonic acid.

The acid with this long name, $C_{10}H_5.NH_2.OH.SO_3H$, was first described by Professor Meldola in 1881. He obtained it by the reduction of nitroso-β-naphtholsulphonic acid (*Chem. Soc. Journ.*, xxxix., 47). It has since been obtained in much larger quantity by Witt, by reducing the orange colouring matter from diazo-benzene chloride and Schaeffer's β-naphthol sulphonic acid (*Annalen Ch. and Ph.*, 152, 298), and he described his process and the characters of the product in the *Proceedings of the German Chem. Society* last December.

It is now produced on the manufacturing scale by the *Actiengesellschaft fur Anilinfabrikation* at Berlin, and may be obtained in the markets, and I think it may be of interest to chemists as well as photographers.

Eikonogen crystallises well from solution in water, and the crystals contain two molecules of water of crystallisation. It dissolves with tolerable facility in hot water, but is only sparingly soluble in cold water, and is insoluble in alcohol. The aqueous solution quickly turns yellow, and gradually brown. An akaline solution turns brown immediately from absorption of oxygen. To keep the aqueous solution for any time it is necessary to add sodium sulphite. Even with the addition of sodium sulphite I have found that it does not remain colourless very long.

I need not say that a great variety of reducing agents may be used as photographic developers, but the most essential quality to secure is that the reducing agent shall quickly reduce those portions of the silver compound which have been exposed to light, but shall have no effect, or no rapid effect, on the silver compound which has not first been acted on by the light; in fact, that the reduction shall extend to the faintest lights, but shall never spread beyond the particles which have received the impulse of light. Of all substances tried, perhaps pyrogallol has held its own the longest, though some prefer ferrous oxalate, and of late hydroquinone has been a good deal used. The chemical action of hydroquinone is very similar to that of pyrogallol, and the fact that the former is paradihydroxybenzene, and pyrogallol is a trihydroxybenzene, led Dr. Andresen, of Berlin, to try the effect of other para-derivatives of benzene which, by oxidation, would easily give quinones or similar substances. Para-diamidobenzene and para-amidophenol were found to be well adapted for developing photographs. Subsequently Dr. Andresen turned his attention to the sulphonic acids, and the outcome has been that eikonogen appears to fulfil the requirements of a good developer the best.

Dr. Andresen claims for it—

1. That while eikonogen reduces the bromide of silver so far as it has been subject to the action of light, the bromide in dry gelatin plates which has not been exposed to light remains unaffected by it.

2. That concentrated solutions of eikonogen (1 : 20 to 1 : 50) produce even with instantaneously exposed plates minutely detailed negatives.

3. The minuteness of detail produced by eikonogen is supposed to be due to the fine grain of the silver precipitate.

4. The tone of the negatives given by eikonogen is well adapted for printing, and in this respect it excels pyrogallol.

5. The solutions of eikonogen containing sodium sulphite are durable even after the addition of carbonate of soda, and the same solution can be used for several pictures in succession.

6. Eikonogen is not poisonous, which cannot be said of pyrogallol or hydroquinone.

The specimens which I exhibit bear out, I think, the claims. The negatives are remarkably perfect in detail, the tone is excellent, blacker than is given by pyrogallol, more delicate than is given by ferrous oxalate, and the prints from them are very good. I need not say that they have been taken by an experienced photographer.

My own experience of eikonogen is, as yet, very limited, and my practice of photography is limited to spectroscopic photography and negatives. It is necessary for me to have a very sensitive developer, which will develop the faintest details and, at the same time, give all the shades of depth which correspond to variation in the brightness of the spectral lines. Hitherto I have not found anything do so well for my purpose as pyrogallol; but eikonogen seems as sensitive as pyrogallol, and at the same time to give me a picture in which the lines are blacker and more easily seen under a microscope. I cannot quite endorse Dr. Andresen's claim that solutions of eikonogen with sodium sulphite are very permanent. The same solution can, however, be used for several pictures in succession. For instantaneous photographs the solution has to be made alkaline with caustic alkali, and then the liquid becomes brown very quickly. For portraits, and such like pictures, an alkaline carbonate, such as sodium carbonate, may be used.

As regards the non-poisonous character of eikonogen, I suspect it can only be due to its sparing solubility, for so powerful a reducing agent can hardly fail to have a strong effect on the animal economy.

* Read before the British Association, Section B, Newcastle Meeting.

ACETYL DERIVATIVES OF CELLULOSE.

By C. F. CROSS and E. J. BEVAN

In recent numbers of the *Berl. Berichte* (1889, 1464 and 2207) Erwig and Kœnigs describe the preparation of a pentacetyl dextrose by the method proposed by A. P. N. Franchimont in 1879 (*Ber.*, xii., 2059), which consists in adding zinc chloride to the anhydride in place of sodium acetate (Liebermann) as the auxiliary.

The acetylation of cellulose by this method was studied by Franchimont, who found that the main product was the triacetyl derivative. The last communication by this author on the subject (*Compt. Rend.*, xcii., 1053) promises a further investigation. Some years have, however, elapsed, and, the matter not having been further advanced, we have thought it expedient to reopen the subject. The method we have followed is as follows:—

The anhydride is heated to the boiling-point, a fragment of zinc chloride dissolved, and the cellulose—specially purified cotton-wool—added in successive small portions. The digestion was continued two to three days. Preliminary observations on the crude product of the reaction, separated on treatment of the filtered solution with water, showed that the acetic acid obtained by saponification was considerably in excess of the quantity obtainable from triacetyl cellulose.

The product was purified by solution in glacial acetic acid, the solution being limpid and not gelatinous as stated by Franchimont in the case of triacetyl cellulose, and filtering. The filtered solution was divided into two parts, one of which was treated with water directly, the precipitated product being washed and dried (*a*); to the other permanganate solution was added in successive small portions, and then water in excess. The flocculent

precipitate was treated with sulphurous acid, finally washed, and dried (*b*). The products—(*a*) crude and (*b*) purified—were analysed, with the following results :—

	(*a*).	(*b*).
C	52·3	51·6
H	5·6	5·8

The carbon percentage calculated for the triacetyl derivative is 50·0, for pentacetyl cellulose 51·6. More conclusive, however, than these numbers are those afforded by the determinations of the acetic acid yielded on saponifying the product. These varied from 79 to 82 per cent with various preparations. The percentages calculated for the tri-, tetra-, and pentacetyl derivatives are respectively 62, 73, and 81. As the evidence stands at present, therefore, the soluble product of the original reaction appears to be a pentacetyl cellulose.

The formation of such a derivative would of course have a very important bearing on the question of the constitution of cellulose, and we therefore reserve any more positive statements as to its composition than are contained in this bare record of experimental results. The results of our continued investigation will form the subject of a fuller communication at an early date.

4, New Court, London, W.C.,
September 19, 1889.

NOTE ON DIFFUSION.

By W. A. DIXON, F.I.C., F.C.S.,
Lecturer on Chemistry, Sydney Technical College.

FROM all text-books put into students' hands they come to very erroneous conclusions on the subject of diffusion, as I have found by experience both in teaching and examining during many years. I am induced to send this note, as I find the usual form of statement in the beginning of Prof. Mendeleeff's lecture in CHEMICAL NEWS, vol. lx., p. 1, just to hand, when he says :—"The fact of the existence of these invisible motions may at once be made apparent by demonstrating the difference in the rate of diffusion through porous bodies of the light and rapidly moving atoms of hydrogen and the heavier and more sluggish particles of air"; and lower down he speaks of diffusion through colloidal substances.

This is, of course, quite correct, but students and those ignorant of the subject always infer that the diaphragm, porous in the case of gases or colloidal in the case of liquids, is *the* point of importance, when actually they have no more to do with diffusion than the diaphragm in the body of a microscope has to do with the magnifying power of the objective.

In text-books usually the first example of diffusion given and illustrated is a vessel of chlorine attached by a tube to a vessel of hydrogen, the latter being uppermost, showing that in a certain time the gases become uniformly mixed against the action of gravity. Students are not told, however, that in this experiment two different actions go to produce the effect. Roughly speaking, the diffusive action of the hydrogen is about six times that of the chlorine; so when six volumes of the former pass into the space occupied by the latter, of which one volume only diffuses, the result is an increase of pressure in the lower vessel and a decrease in the upper. The vessels being in free communication, the pressure is instantly adjusted by a flow of mixed gases from the lower to the upper as a current. This being explained, the action of a diaphragm comes simply into play as preventing the passage of the current without interfering with the diffusive action, and Graham's molecular sieve is at once understood. The diaphragm cuts off current in either liquid or gaseous diffusion as the microscope diaphragm cuts off aberration.

In connection with this the statement is often made that, a vessel being filled with one gas, another gas introduced occupies the whole space as if it were a vacuum, without one word about increase of pressure or volume, which leads to some curious misconceptions on the part of even well-educated intelligent people.

CLASSIFICATION OF THE ATOMIC WEIGHTS IN TWO ASCENDING SERIES, CORRESPONDING TO THE GROUPS OF ARTIADS AND PERISSADS.*

By W. R. LIVERMORE, Major of Engineers, U.S. Army.

IF the atomic weights of all chemical elements are arranged in a single ascending series, it will take the following form if expressed in whole numbers :—

1,—7, 9, 11, 12, 14, 16, 19,—23, 24, 27, 28, 31, 32, 35,—39, 40, 44, 48, 51, 52, 55, 56, 59, &c. ;

corresponding to the elements,—

H,—Li, Be, B, C, N, O, F, —Na, Mg, Al, Si, P, S, Cl,—K, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, &c.

The well-known "Law of Octaves" calls attention to the fact that each element bears a strong resemblance to that seven places from it in this series, and the "Periodic Law" states that the properties of elements stand in periodic relation to their atomic weights. These laws have been enunciated and illustrated by Newlands, Mendeleeff, Lothar Meyer, and others, and are now familiar to all students of chemistry.

Referring to these laws, Wurtz, in his "Atomic Theory," says :—"Though it may be generally true that the properties of bodies are subject to periodic modifications with the increase of their atomic weights, the law of these modifications escapes our observation, and seems to be of a complicated nature; for on the one hand, the atomic weights of successive elements vary within considerable limits without displaying any regularity in these variations; on the other hand, we must confess that the gradations of properties—in other words, the greater or less divergences between properties of successive elements—do not appear to depend upon the degree of the differences between the atomic weights. These are real difficulties."†

Lothar Meyer on the same general subject says :—"There can be no doubt as to the fact that these differences are subject to law";‡ and, "There is still much work for the hands and mind; but it will be thoroughly rewarded. The prize is a systematic inorganic chemistry which will bear comparison with the thoroughly developed system of organic chemistry."§

The object of this paper is to contribute to the removal of these difficulties, by showing that the increase in the atomic weights of the elements follows a law of the utmost simplicity in its general form, and identical with that of the series of organic compounds.

Let us take the series above mentioned and consider whether any of its terms can be classed in a series of constant increase. Beginning with 2 as a modulus, we find that it applies to 7, 9, and 11, with no recurrence of this difference except for the terms 12, 14, 16; 3 applies only to 9, 12,—24, 27,—48, 51, and to 16, 19 * * 28, 31 * * * * * 52, 55; 4, however, applies to 7, 11 * 19, 23, 27, 31, 35, 39 * * 51, 55, 59, and to 12, 16 * 24, 28, 32 * 40, 44, 48, 52, 56; thus embracing in two parallel series all the terms of the first three periods of Newlands and Mendeleeff, with the exception of 9 and 14, *i.e.*, 22 out of 24. The probability that these numbers would so far

* A Paper presented to the American Academy of Arts and Sciences April 10, 1889.

† "The Atomic Theory," 1881, p. 162.

‡ "Modern Theories of Chemistry," English Translation, 1888, p. 160.

§ *Ibid.*, p. 170.

coincide with the regular series from the result of chance is too slight to be entertained. If now, in addition to this coincidence, any points of resemblance can be discovered among several of the elements in each series, such resemblances are significant; but when it appears that all, or nearly all, in each series fall into a distinct group that has already been recognised as such by chemists, there is scarcely room for doubt that the regularity of the series is connected with the intrinsic nature of the elements.

Those of the first series are all perissads, and those of the second artiads, or elements of uneven and even quantivalence respectively, with the single exception in one case of scandium, a newly discovered element whose atomic weight has never been so accurately determined as to throw it out of its group, and cobalt and nickel, which apparently belong to another group. For the present, therefore, the law of regular increase in the atomic weight of the parallel series is spoken of as the law of artiad and perissad increase, or more briefly as the Perissad Law.

By similar methods, we find that the numbers between 70 and 100 fall naturally into two series, with the common difference of 5 for the perissads and perhaps 4 for the artiads. The latter series, however, is somewhat indefinite.

Between 100 and 150 the perissads increase regularly, with a common difference of about 6½, and the artiads less regularly, with the same difference, as shown in Tables I. and II.

Too little is known of the atomic weights between 150 and 190, and of those above 210, to justify their classification. Between 190 and 210 we find that 4 applies to 195, 199 * 207, and to 196, 200, 204, 208.

All of the first series are artiads, and in the second all except 200, or Hg, are recognised as perissads, and this element is so similar in many respects to Cu, Ag, and Au that for the present it is allowed to remain in its place. There only remain unclassified, 9, 14, 59, 104, and 193. Of these numbers, 9 is the atomic weight of Be and appears to differ too much from 8, the serial number of this element, to be recognised in its natural place.

The remaining numbers, 14, 59, 104 * 193, form a series by themselves, with a difference of a little less than 45. Ni and Co correspond to 59, Ru and Rh to 104, and Ir to 193. These elements are always classified together, and this regularity of increase has often been noticed. But perhaps 14 or N falls into this series accidentally.

In Tables I. and II. the first column shows the symbols for the elements; the second column, the serial numbers derived from the formula; the third column, the observed atomic weights; and the fourth column, the deviations from the serial numbers. The next columns show the specific gravity, the atomic volume, the fusibility, malleability, and place in an electro-chemical series for each element, and the last column, the group in the classification of Newlands and Mendeleeff to which the element has been assigned. The horizontal lines divide the series and periods of this system.

The observed atomic weights are taken from the lists of Clarke,* L. Meyer,† and Van der Plaats,‡ and in most cases by selecting for each element that one of the values that differs least from the mean, taking oxygen at 16 for a standard, and expressing but one place of decimal fractions. The data for the next four columns are taken from Meyer's "Modern Theories." To express their fusibility, the elements are divided into seven classes, that represented by 1 being the most fusible. The brittle and malleable elements are distinguished by the initial letters B and M. In the electro-chemical series, taken from Barker's "Text-book of Chemistry,"§ 1 is the most electro-positive in an acid solution, and 63 the most negative.

It appears from these tables that none of the deviations from the serial numbers exceed 0·6 excepting that for Cb among the perissads, and Zn and Mo among the artiads; Zn differs by just a unit, and seems to form an exception to the regularity.

In his account of the Discovery of the Periodic Law,* Newlands points out the irregularity of the single series, illustrating it by several tables, and the data are clearly set forth and tabulated in a recent paper by Venable, on the "Re-calculation of the Atomic Weights."†

In the artiad grand group no atomic weight corresponds to 20, 36, 83, or 131, and a reference to the electro-chemical series will show that these are the points at which the elements change from a negative to a positive maximum, corresponding also to the maximum atomic volumes, and to the end of the Mendeleeff periods.

These points are marked with asterisks in the table.

Analogy points to the possibility of elements with atomic weights of 15, 43, or 44, 47, 60, and perhaps of 99, 100, and 143·5.

The newly discovered philippium and praseodymium may perhaps correspond to 47 and 143·5, respectively, but there appears to be no place in either series for neodymium, or 140·3.

TABLE I.—*Perissads.*

El.	Atomic Weights. Ser.	Obs.	Dev.	Physical Properties. Sp. gr.	At. vol.	Fus.	Mal.	Elec.	Gr.
H	1	1·0	0·0	—	—	—	—	—	I.
	$+6+n\times4$								
Li	7	7·0	0·0	0·59	11·9	1	M	5	I.
B	11	11·0	0·0	2·68	4·0	6	B	49	III.
	15	?							
F	19	19·0	0·0	—	—	1	B	60	VII.
Na	23	23·1	+0·1	0·97	23·7	1	M	4	I.
Al	27	27·1	+0·1	2·56	10·6	3	M	13	III.
P	31	31·0	0·0	2·30	13·5	2	B	55	V.
Cl	35	35·5	+0·5	1·38	25·6	1	B	59	VII.
K	39	39·1	+0·1	0·86	45·4	1	M	3	I.
Sc	43	44·?	—	—	—	—	—	—	III.
	47	?							
V	51	51·3	+0·3	5·50	9·3	7	B	52	V.
Mn	55	55·0	0·0	8·00	6·9	5	B	19	VII.
Co?	59	(59·0	0·0	8·50	6·9	5	M	23)	
Cu	63	63·5	+0·5	8·80	7·2	3	M	31	I.
	$+7+n\times5$								
Ga	70·0	70·0	0·0	5·96	11·7	1	?	?	III.
As	75·0	75·0	0·0	5·67	13·2	2	B	54	V.
Br	80·0	80·0	0·0	2·97	26·9	1	B	58	VII.
Ro	85·0	85·4	+0·4	1·52	56·1	1	M	2	I.
Y	90·0	89·8	−0·2	—	—	—	—	11	III.
Cb	95·0	94·2	−0·8	6·27	15·0	7	B	44	V.
	100·0								
	$+7\cdot5+n\times6\cdot25$								
Ag	107·5	107·9	+0·4	10·50	10·2	3	M	32	I.
In	113·7	113·7	0·0	7·43	15·3	1	M	27	III.
Sb	120·0	120·1	+0·1	6·70	17·9	2	B	47	V.
I	126·3	126·8	+0·5	4·94	25·6	1	B	57	VII.
Cs	132·5	132·9	+0·3	1·88	70·6	1	M	1	I.
La	138·8	138·8	0·0	6·20	22·3	3?	—	18	III.
Di	145·0	145·0	0·0	6·50	22·3	3?	—	17	V.
	$?+n\times4$								
Au	196·0	196·6	+0·6	19·30	10·2	3	M	40	I.
Hg	200·0	200·2	+0·2	13·59	14·7	1	M	33	II.
Tl	204·0	204·2	+0·2	11·86	18·1	2	M	24	III.
Bi	208·0	208·0	0·0	9·82	21·1	2	B	29	V.

* "The Constants of Nature." "A Re-calculation of Atomi Weights," 1882.
† "Modern Theories of Chemistry," English Translation, 1888.
‡ "Verification of the Atomic Weights of M. Stas."
§ "Text-book of Chemistry," p. 16.

* "The Periodic Law," p. 27.
† *Journal of Analytical Chemistry*, January, 1889, p. 48.

TABLE II.—*Artiads.*

El.	Atomic weights. Ser.	Obs.	Dev.	Physical Properties. Sp. gr.	At. vol.	Fus.	Mal.	Elec.	Gr.
	$12 + n \times 4$								
		?							
C	12·0	12·0	0·0	0·33	3·6	7	B	54	IV.
O	16·0	16·0	0·0	—	—	1	B	63	VI.
	20·0	*							
Mg	24·0	24·0	0·0	1·74	13·8	3	M	9	II.
Si	28·0	28·1	+0·1	2·49	11·2	6	B	42	IV.
S	32 0	32·1	+0·1	2·04	15·7	1	B	62	VI.
	36·0	*							
Ca	40·0	40·0	0·0	1·57	25·4	2	M	8	II.
	44·0	?							
Ti	48·0	48·1	+0·1	—	—	—	B	43	IV.
Cr	52·0	52·3	+0·3	6·80	7·7	5	B	53	VI.
Fe	56·0	56·0	0·0	7·80	7·2	5	M	21	VIII.
	60·0	?							
Zn	64·0	65·0	+1·0	7·15	9·1	2	M	20	II.
	$+ 7 + n \times 4$								
Ge	71·0	?	—	?	—	?	—	?	IV.
As	75·0	75·0	0·0	5·67	13·2	2	B	54	V.
Se	79·0	79·0	+0·0	4·60	17·1	1	B	56	VI.
	83·0	*							
Sr	87·0	87·5	+0·5	2·50	34·9	2	M	7	II.
Zr	91·0	90·6	−0·4	4·15	21·7	6	B	14	IV.
Mo	95·0	95·9	+0·9	8·60	11·1	6	B	51	VI.
	99·0	?							
	$+ 7 + n \times 6{\cdot}25$								
Pd	106·0	106·0	0·0	11·50	9·2	4	M	34	VIII.
Cd	112·2	112·2	0·0	8·65	12·9	2	M	25	II.
Sn	118·5	118·0	+0·5	7·29	16·1	2	M	28	IV.
Te	124·8	125·0	−0·2	6·25	20·2	2	B	46	VI.
	131·0	*							
Ba	137·2	137·1	−0·1	3·75	36·5	2	M	6	II.
Ce?	143·5	?	?	6·70	21·0	3?	—	16	IV.
	$? + n \times 4$								
Pt	195·0	194·9	−0·1	21·50	9·1	5	M	37	VIII.
Os	199·0	198·9	−0·1	22·50	8·7	5	B	39	VIII.
	203·0	?							
Pb	207·0	206·9	−0·1	11·38	18·1	2	M	26	IV.
	$14 + n \times 44{\cdot}8$								
Ni	58·8	58·7	−0·1	8·80	6·7	4	M	22	VIII.
Co	58·8	59·0	+0·2	8·50	6·9	5	M	23	VIII.
Ru	103·6	104·0	+0·4	12·26	8·4	5	B	35	VIII.
Rh	103·6	104·2	+0·6	12·10	8·6	5	M	36	VIII.
	148·4	?							
Ir	193·2	193·0	−0·2	22·46	8·6	5	B	38	VIII.

In each of the grand groups, perissads and artiads, the breaks between the minor groups of common difference occur at, or near, the minimum points of the series of atomic volumes, and therefore midway between the dividing lines above mentioned.

The first term of each of the groups of common difference, except the first, viz., Ga, Ag, Au, Ge, Pd, and Pt, appears to be a heavy malleable metal, electrically neutral, and with an atomic volume a little above 9 in the artiad, and 10 in the perissad groups.

With the increase of atomic volume is generally associated an increase in electro-negative properties, and, as a rule, the elements become fusible, brittle, and diamagnetic.

With the maximum atomic volume, the elements change from the extreme of negative to positive, from diamagnetic to magnetic, from brittle to malleable; and with the decrease of volume they lose their electro-positive properties, and, as a rule, become at last brittle and infusible.

The study of the periodic law has directed attention to the relations between the atomic weights and these properties, many of which were previously treated as functions of the electro-chemical order.

When the exact atomic weights are all determined with sufficient accuracy, it is natural to infer that the deviations from the regular increase will show a law as significant as the approximate coincidence with the serial numbers, and even now we see clear evidences of this law. To make it more apparent, it will first be necessary so to adjust the formula as to reduce these differences to a minimum, and in the low atomic weights to take account of smaller fractions.

The formula $a + n\,d$ then has the following values for the several groups of common difference:—

$6{\cdot}99 + n \times 4{\cdot}02$	$12{\cdot}00 + n \times 4{\cdot}01$
$70{\cdot}25 + n \times 4{\cdot}85$	$74{\cdot}88 + n \times 4{\cdot}12$
$107{\cdot}85 + n \times 6{\cdot}20$	$105{\cdot}98 + n \times 6{\cdot}22$

(To be continued).

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING AUGUST 31ST, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, September 6th, 1889.

SIR,—We submit herewith the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from August 1st to August 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Two samples, out of the 175 examined, manifested a "very slight turbidity." The remaining 173 samples were found to be clear, bright, and well filtered.

The improvement in the London Waters, to which we referred in our Report for last month, was well maintained during August. This is seen by comparing the oxygen required to oxidise the daily samples of the water as supplied by the several Companies:—

Oxygen (Per Gallon) Required to Oxidise the Organic Matter.

	July.	August.
New River Company	0·024	0·019
East London Water Company ..	0·045	0·036
Thames-derived Water Companies	0·040	0·037

These details by the oxygen process are fully corroborated by the estimations of the Organic Carbon and Nitrogen which are duly recorded in the tables.

The results generally of our daily examinations, show

the water as supplied by the several Companies to be entirely satisfactory.

We are, Sir,

Your obedient Servants,

William Crookes.
William Odling.
C. Meymott Tidy.

DETERMINATION OF CARBON IN THE IRONS OF COMMERCE.

By L. BLUM.

Under this title L. L. de Koninck recently published a communication recommending, before the combustion of the residual carbon with chromic acid and sulphuric acid, to introduce into the combustion-flask a little silver sulphate in order to convert any chlorine compounds which might have escaped removal by washing into insoluble silver chloride.

Koninck's assumption on which this proposal is based, *i.e.*, that the silver chloride formed is not attacked by the mixture of chromic and sulphuric acid, is in full contradiction to other authors. A. Sauer (*Zeitschrift Anal. Chemie*, vol. xii., p. 176) decidedly contradicts the assumption that silver chloride is scarcely, if at all, attacked by concentrated sulphuric acid. He observed that it is completely dissolved and decomposed, with the escape of hydrochloric acid. In an editorial note on Sauer's memoir we find it stated that, according to A. Vogel, boiling oil of vitriol slowly dissolves silver chloride, with escape of hydrochloric acid and formation of silver sulphate. According to Volhard (*Zeitschrift*, xviii., p. 281), sulphuric acid diluted with half its volume of water does not attack silver chloride. This, however, is a degree of dilution which never occurs in the combustion of the carbon in irons.

To arrive at certainty the author performed the following experiments:—

50 c.c. concentrated sulphuric acid were mixed with a drop of hydrochloric acid, well shaken up, and a drop of the solution of silver nitrate was then added. There appeared a white precipitate of silver chloride, which was completely dissolved on boiling. The liquid was set aside in the cold until the next day, but it remained clear. Testing for chlorine gave a negative result; the silver chloride had, therefore, been completely dissolved by boiling with concentrated sulphuric acid, with expulsion of hydrochloric acid.

The following experiment bears more directly upon the proposal of De Koninck:—

The combustion-flask of an apparatus for determining carbon in iron was charged with an unweighed quantity of silver chloride, about 10 grms. chromic acid, and 100 c.c. concentrated sulphuric acid. The silver chloride had been prepared by precipitating a few drops of hydrochloric acid with excess of silver sulphate, so that no chlorine was present except in combination with silver. The water used in rinsing the silver chlorine into the flask was about 20 c.c. In conducting the experiment all precautions were observed which are recommended for the determination of carbon by combustion with chromic acid and sulphuric acid. As a recipient was used a Geissler absorption apparatus filled with potassa-lye. It weighed—

After the experiment	68·3165 grms.
Before ,, ...	68·0670 ,,
Increase..	0·2495 ,,

Between the combustion-flask and a washing-bottle filled with concentrated sulphuric acid there was interposed a U-shaped bulb-tube as a refrigerator. In it there had been condensed during the operation a small quantity of water. On being acidulated with nitric acid and mixed with silver nitrate it weighed, after ignition, 0·0098 grm.

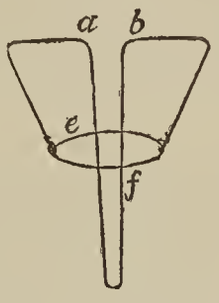
According to these experiments the proposal of De Koninck appears utterly useless.—*Zeitschrift f. Anal. Chemie* (Vol. xxviii., Part 4, pp. 450—452).

FILTERING ARRANGEMENT.

By C. R. GYZANDER,
Chemist, Cochrain Chemical Co., Boston, Mass., U.S.A.

A filter support, which is an improvement on the arrangement for rapid filtration described by Mr. R. A. Fessenden in the Chem. News, vol. lx., p. 102, is shown in accompanying sketch. It is made from platinum wire, copper wire, or any other suitable material, and bent in the shape shown in Fig 1.

Fig. 1.



A paper, folded as described by Mr. Fessenden, is pushed in between the wires *a* and *b*, Fig. 1, which serves the same purpose as the glass rod, that is to support the inner folds of the filter; whereas the ring *c f* supports the outer folds, giving the whole an appearance of a paper formed with two compartments. This may now be placed in a glass funnel, or used alone, simply by

Fig. 2.

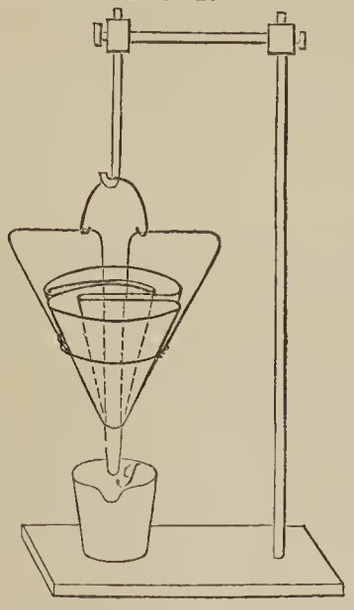


Fig 3.

suspending it over the beaker as in Fig. 2, the liquid following the wire and dripping from the point *g*.

As a means of drying precipitates on the filter, it is far superior to the old way of placing the glass found with its filter in the drying oven, as the air has access to the paper from all sides, whereby it dries much more rapidly and thoroughly. For a 7½-inch filter, a support of $\frac{1}{32}$-inch platinum wire, with the ring *c f*, 2½ inches in diameter, and the wires *a* and *b*, 3 inches long, gave excellent service. A glass rod bent as indicated by Fig. 3 works very well.

SODIUM NITROPRUSSIDE AS A REAGENT FOR CAUSTIC ALKALIES AND ALKALINE EARTHS.

By H. BRUNNER.

Whilst engaged in another investigation the author observed that sodium nitroprusside, if mixed with caustic soda or potassa, produces an intense yellow colouration. Baryta- or lime-water react in the same manner, whilst soluble carbonates and bicarbonates have no effect. Hence it appears that sodium nitroprusside is not merely a reagent for soluble metallic sulphides and sulphhydrates, but also for soluble metallic oxides and hydrates.

If an aqueous solution of sodium nitroprusside is mixed with sodium hydrate until an orange colour appears and alcohol is then added, after shaking and settling a deep yellow oil is separated out, which, on prolonged standing, solidifies into fine orange-coloured crystals. A watery solution of this sodium salt, the composition of which has not yet been determined by the author, gives coloured precipitates with metallic salts. The soda salt serves as a reagent for acids, with which its solution gives a green colour, which, on exposure to the air, turns violet, and finally gives a green precipitate.—*Schweitzer Wochen Pharmacie* and *Chemiker Zeitung*.

ANALYTICAL STUDIES ON PHOSPHODODEKAMOLYBDIC ACID, THE CONDITIONS OF ITS FORMATION, AND ITS SEPARATION AS AN AMMONIUM SALT.

By Dr. Franz Hundeshagen.

The conditions of the formation of yellow phosphomolybdic acid and its complete separation as an ammonium salt, although of the highest analytical importance, are as yet but superficially known. The execution of Sonnenschein's process in its various applications and modifications is therefore often involved in difficulties, and often does not lead to an accurate result, especially when it is required to separate and determine very small quantities of phosphoric acid. It is, therefore, worth while to examine the causes which may have a disturbing effect in the precipitation of phosphoric acid by molybdic acid, and to establish methodically the conditions which lead to uniform and trustworthy results.

1. *Influence of the Nature of the Solution upon the Composition of the Precipitate.*

The author finds the composition of the precipitates obtained under the most varying conditions (if only free from free molybdic acid and other impurities), after washing with cold dilute nitric acid and drying at 130°—150°, to have in all cases the formula $12MoO_3.PO_4.(NH_4)_3$, whether the precipitation had been effected in strongly or slightly acid nitric, hydrochloric, or sulphuric solutions containing more or less ammoniacal salt, dilute or concentrate, hot or cold solutions; and whether phosphoric or molybdic acid was present in excess, or if the solution contained foreign salts (*e.g.*, potassa) or not.

The precipitate obtained with excess of acid, washed with cold dilute acid, and dried in the desiccator over calcium chloride and caustic potassa until the weight became constant, contained, according to the acid in the presence of which the precipitation ensued, and which served for washing two mols. NO_3, H, or ClH with one mol. H_2O, probably in an unstable chemical combination. Both acid and waterwere partially expelled at a moderate heat, but quickly and completely at temperatures exceeding 130°.

In determining the phosphoric acid and the molybdic acid, the author used the compound dried between 130° and 150°. The molybdenum was determined not as sulphide, but as MoO_3, as it was difficult to obtain a sulphide of constant composition. After the phosphoric acid had been separated in the ordinary manner by means of magnesia mixture, sulphuretted hydrogen was passed into the ammoniacal filtrate until the liquid had assumed a bright red colour. All the molybdic acid was then precipitated as sulphide by the addition of hydrochloric acid, not a trace remaining in solution. The sulphide was then persistently washed with water containing sulphuretted hydrogen and hydrochloric acid, rinsed down from the filter into a broad platinum capsule; the residue adhering to the filter was oxidised by the vapour of bromine, dissolved in water, and added to the main portion. After careful stirring and repeated evaporation with a mixture of dilute sulphuric and nitric acids, driving off the acids by heat, and carefully igniting the residue to very dull redness, all the sulphide was oxidised to molybdenum trioxide. In order to expel any residues of sulphuric acid and to prepare the substance for weighing, it was transferred to a platinum crucible, the capsule was washed with dilute ammonia, and the solution poured into the crucible. By cautious evaporation, very gradual heating, and final ignition to dull redness, the molybdic acid was obtained pure. It appeared as a dense powder—bright yellow when hot, almost white when cold—and after cooling in the exsiccator it was weighed.

The direct determination of the ammonia by distilling the phosphomolybdate with soda-lye and titrating the distillate gave no satisfactory results. An indirect determination by saturating the salt with standard ammonia or soda was found to be practicable and convenient. By means of this method, which will be described in full in the sequel, the acids present in unstable combination were determined.

The proportion of phosphoric acid in the precipitate dried at 150°, of different preparations, and found on microscopic examination to contain no free molybdic acid, fluctuated between 3·72 and 3·77 per cent. The molybdenum trioxide was found 91·86 to 92·11. The formula $12MoO_3.PO_4.(NH_4)_3$ would require 3·78 P_2O_5 and 91·75 MoO_3 (O = 16, Mo = 96).

In accordance with these values the weight of an ammonium phosphomolybdate, ascertained by a method to be described below and dried at 150°, obtained by precipitating a known weight of phosphoric acid by 24 mols. or an excess of molybdic acid, amounted to 26·90 to 26·65 times the weight of the phosphoric acid employed, corresponding to a proportion of 3 72 to 3·75 per cent, which was in two cases confirmed by analysis, the weight obtained being 3·74 per cent P_2O_5.

The precipitates thrown down with an excess of acid, washed with diluted acid, and dried for several weeks in the exsiccator over calcium chloride and caustic potassa until the weight was constant, lost, when heated to 130° to 150° (giving off moist strongly acid vapours), in weight.

The nitric acid compound, 7·13 per cent = 7·67 per cent, on the substance dried at 150°.

The hydrochloric compound, 4·78 per cent = 5·02 per cent, on the substance dried at 150°.

For saturating the precipitate obtained with nitric acid were required for salts dried in the exsiccator 23·03 per cent, corresponding to 25 43 mols., or 53·89 NaOH corresponding to 25·28 mols. After heating to 150°, 20·96 per

cent NH_3, corresponding to 23·14 mols., or 50·01 per cent NaOH, corresponding to 23·46 mols. (All referred to 1P).

The salt precipitated by hydrochloric acid was neutralised, when dried in the exsiccator, by 54·01 per cent NaOH = 25·34 equivs.; after heating to 150° by 49·92 NaOH = 23·42 equivs.

These numbers, for the sake of direct comparison, have been re-calculated for the dry substance free from acid. Triammoniumphosphododekamolybdate would require for saturation 23 equivs. of alkali.

As we see, the precipitates dried in the exsiccator require for neutralisation about two equivalents more alkali than those dried at 150°, corresponding to as many equivalents of nitric or hydrochloric acid in combination with the phosphomolybdate. In point of weight 2 mols. NO_3H would amount to 6·71 per cent, and 2 mols. HCl to 3·89 per cent if referred to 100 parts of phosphomolybdate free from acid and water. If the numbers found as loss of weight on heating to 150°, the salts previously dried in the exsiccator, are diminished by these amounts, there remain for water 7·67−6·71=0·96 per cent and 5·02−3·89=1·13 per cent, of which figures the former represents exactly, and the latter approximately, a mol. of water. The precipitate dried in the exsiccator has consequently, according to the acid used in its precipitation and washing, the composition—

$$12MoO_3.PO_4.(NH_4)_3.2NO_3H.H_2O \text{ or}$$
$$12MoO_3.PO_4.(NH_4)_3.2ClH.H_2O.$$

The author has not made a determination of the proportion in the precipitate, as the compound, if washed, neutrally undergoes a change if it remains any length of time in a moist condition.

2. *Influence of the Proportion of Ammonium Salt (Nitrate) in the Solution upon the Separation of the Precipitate.*

For these experiments the following standard liquids were employed:—

Solution A.—5·043 grms. sodium hydrophosphate per litre, therefore 0·001 grm. P_2O_5 per c.c.

Solution B.—Neutral sodium molybdate, 0·010 grm. per c.c.

Solution C.—Ammonium nitrate, 0·010 NO_3NH_4 per c.c.

Solution D.—Nitric acid, 0·10 grm. NO_3H per c.c.

Of the solutions A and B known volumes were mixed, so that phosphoric and molybdic acid were present in some experiments in the molecular proportion 1 : 24, or in some cases in a different proportion. In some cases the solution was further concentrated by evaporation, and in others diluted by the addition of water. A measured quantity of the nitric acid D was then added, the yellow liquid was heated almost to a boil, and a solution of ammonium nitrate was very gradually run in, stirring all the time with the glass rod until the precipitate of ammonium phosphomolybdate no longer increased.

During the formation of the latter the following phenomena were observed:—At first the precipitate disappeared again regularly if the observer waited a short time after the addition of every drop of ammonium nitrate. It did not become permanent until a considerable part of the solution had been added, though it still increased visibly with every drop of the ammonium salt added, and soon gave the solution a pale yellow, milky appearance. In this state, which resembled an emulsion, the liquid did not clear in the slightest, even after prolonged heating, and on the attempt to filter it ran through very turbid.

But now a few more drops of the ammonium nitrate generally sufficed to condense the precipitate and to cause it in time to deposit, so that the solution, if viewed against a blue glass, appeared clear. Further addition of ammonium nitrate occasioned no precipitation; the separation of the phosphomolybdic acid was completed, and the solution quite colourless.

The quantity of ammonium nitrate consumed was noted, the final volume of the liquid determined, and it was calculated how much ammonium nitrate was present in 100 c.c. of the solution. It now appeared that this quantity, within the limits of the experiment, independently of the proportion of phosphoric, molybdic, and nitric acids, was always essentially the same, *i.e.*, about 0·4 to 0·5 grm. ammonium nitrate in 100 c.c. If the quantity was smaller than 0·4 grm. the liquid remained milky and could not be filtered. With more than 0·5 grm. in 100 c.c. the separation of the phosphomolybdic acid (unless the solution contains less than 0·01 grm. phosphoric acid per 100 c.c.) in a number of minutes, the more rapidly the more phosphomolybdic acid was present.

In order to effect the most rapid separation of the phosphomolybdate, it seemed most convenient to have from 5 to 10 per cent of ammonium nitrate.

In a similar manner the quantity of potassium nitrate necessary for the precipitation of the phosphododekamolybdic acid as a potassium salt was determined. It was found that the precipitation (apparently independent of the other conditions) is not complete until the liquid contains 1·76 grm. NO_3K in 100 c.c. To throw down the phosphomolybdic acid there are required—

$$\frac{1{\cdot}76}{101} : \frac{0{\cdot}45}{80},$$

or about three times as many mols. potash salt as mols. ammonium salt.

It was interesting to know the influence of the relative proportions of ammonium and potassium salt in the solution upon the composition of the precipitate.

3. *The Conditions of Temperature and Concentration.*

These conditions have been but little studied. In accordance with Stünkel, Wetzke, and Wagner, the author found that under otherwise favourable conditions the temperature had no influence upon the completeness of the separation of the phosphomolybdate. The precipitation was the more rapid the more of the elements of phosphomolybdic acid was present and the more strongly it was heated.

Thus, in solutions which contained not more than 0·05 grm. P_2O_5 in 100 c.c., the precipitate fell down almost instantly on heating to near the boiling-point and adding solution of molybdic acid, whilst in the cold a precipitate appeared, indeed, at once, but required for its complete separation from half an hour to an hour.

0·010 grm. P_2O_5 in 100 c.c. of liquid which were completely precipitated from a hot solution in a few minutes, formed at common temperatures the first traces of a precipitate in the shape of delicate stripes and veils on the sides of the glass after the solution had stood for ten minutes with frequent stirring. (How considerable may be the influence even of slight differences of temperature is shown by the observation that these cloudings appear most plainly at those parts of the side of the vessel at which the heat of the body has been communicated to the liquid by contact with the hand). The separation then became slowly more copious, and was almost complete in two and a half hours. But even after twelve hours traces of phosphomolybdic acid remained in solution, and their separation had to be assisted by heat and agitation.

Stirring and rubbing with the glass rod, promote, in all cases the separation. Under certain circumstances this mechanical impulse is necessary to set up the reaction.

As for the physical properties of the precipitates obtained at different temperatures and under other varying conditions, those thrown down from very hot and not too acid solutions and with an excess of molybdic acid seemed to the author, on microscopic examination, the most perfectly crystalline. The presence of a sulphate seems to favour the crystalline development of the precipitate, but delays its separation.

The precipitate from a cold solution is composed of

spheroidal granules of very different sizes. That from hot solutions is very uniform in its grain and consists of distinctly formed octohedrons.

This is the reason why the precipitate from a hot solution settles more quickly and more completely and can be more easily filtered and washed without loss than that thrown down in the cold, whose finest particles can remain for a long time in suspension, and can pass through the pores of the filter.

4. *Influence of the Degree of Acidity of the Solution upon the Formation of the Phosphododekamolybdate.*

If we allow dilute nitric acid gradually to flow into a neutral solution containing the elements of phosphododekamolybdic acid along with a suitable quantity of ammonium nitrate, applying heat, we observe the following phenomena :—

In the first place the liquid remains completely clear and colourless, but, on the further addition of acid, there appear yellow colourations and turbidities, which, on stirring, disappear in a short time. Then follows a permanent yellow colour, at first pale, but becoming more and more intense, with incipient precipitation, then copious yellow deposits which subside at first slowly, but more and more perfectly on further acidification. Finally, a visible precipitation is no longer produced, but there still ensue in the liquid, as it becomes clear, slight deposits. After a few more drops the separation of the yellow phospho-molybdate is complete.

A further slight addition has no influence on the precipitate, but a considerable excess produces a decomposition the more decided the greater the excess.

More manifest is this decomposing action of an excess of acid if it is allowed not to act upon the pre-formed phospho-molybdate, but is added to the phosphoric or the molybdic solution before they are mixed together.

Whilst in a solution of a proper degree of acidity P_2O_5 is thrown down quantitatively by 24 mols. MoO_3; in strongly acidified solutions double the quantity, and more of molybdic acid may be consumed before any precipitation appears. Not until the injurious excess of acid has been neutralised does the liquid deposit all its phosphomolybdic acid, which had previously existed in a dissociated condition. The dissociated phosphomolybdic acid can also be caused to separate by an excess of molybdic acid, which must be the larger the more acid the liquid.

(To be continued).

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

In a report presented to the Bath Meeting the Committee gave an account of the replies they had received to a letter addressed to the head masters of schools in which elementary chemistry is taught. In this letter the Committee had asked for a report on the chemical teaching, and also for a statement as to the methods which had been found to render the teaching most effective as a mental training. In commenting on these replies the Committee pointed out that the evidence which had been collected was conclusive in showing that much of the teaching of elementary chemistry is far from satisfactory, and needs to be considerably modified if it is to effect that valuable mental discipline which science teaching can afford.

The Committee are convinced that the high educational value of instruction in physical science has never been exhibited to its full advantage in most of our educational institutions. Nevertheless there exists already a considerable body of experience which proves that there is no more effective and attractive method of training the logical faculties than that which is afforded by a properly arranged course of instruction in physical science; by no other means are the powers of accurately ascertaining facts, and of drawing correct inferences from them, so surely developed as they are by the study of this subject.

Since the last meeting the Committee have been actively engaged in discussing the lines which a course of elementary instruction in chemistry should follow. The Committee were the more inclined to offer suggestions of their own, since they had learnt from the replies made to their letter of last year, by teachers in many of our well-known schools, that not only is the necessity for the adoption of improved methods fully recognised, but that teachers are anxious to receive advice and assistance in introducing them.

It cannot be too strongly insisted that elementary physical science should be taught from the first as a branch of mental education, and not mainly as useful knowledge. It is a subject which, when taught with this object in view, is capable of developing mental qualities that are not aroused, and indeed are frequently deadened, by the exclusive study of languages, history, and mathematics. In order that the study of physical science may effect this mental education, it is necessary that it should be employed to illustrate the scientific method of investigating nature, by means of observation, experiment, and reasoning with the aid of hypothesis; the learners should be put in the attitude of discoverers, and should themselves be made to perform many of the experiments. The lessons ought to have reference to subjects which can be readily understood by children, and illustrations should be selected from objects and operations that are familiar to them in everyday life. Chemistry is particularly well adapted for affording this kind of instruction, and the Committee are of opinion that a course which is mainly chemical will be most useful in developing logical habits of thought.

Chemical inquiry involves, however, the use of various physical processes, and these are themselves of great value from the point of view from which the instruction is being given. It is also of great importance that the learners should become acquainted with the characteristic instrument of physical science, viz., measurement, and therefore quantitative processes should be largely made use of.

Having agreed as to the general principles on which a scheme of elementary instruction in chemistry should depend, the Committee gladly accepted the offer of Professor Armstrong to draw up an account of such a scheme in sufficient detail to serve as a guide to those who have to provide such teaching. Without pledging themselves to accept all its details the Committee consider that the scheme which Professor Armstrong has prepared (see below) is in general accordance with their views as to what should constitute a course of elementary instruction in physical science.

With regard to the manner in which the scheme should be carried out, the Committee wish to lay stress on the following points. In order that the plan should produce its full educational effect, the instruction should be commenced at an early age, and be extended to every child in the school. They do not desire to bring forward physical science as a substitute for any of the other principal subjects of study, but they ask that, like these subjects, it should be looked upon everywhere as a necessary part of education, and that it should receive a due share of the time devoted to school work. It is well known that at present science-teaching does not generally receive as much time and attention as is given to other studies,

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe, Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

This was made clear in the report of the Committee last year. It will be necessary to allot more time to the subject, and to employ a greater number of teachers. A teacher should not be required to give practical instruction to more than from fifteen to twenty pupils at one time, although the classes at lectures and demonstrations might be somewhat larger.

While the scheme now proposed may involve the employment of a larger number of teachers of natural science, on the other hand fittings and apparatus of the simplest description are all that will be absolutely needed, and the cost of maintenance will be relatively small.

The Committee are aware that the course of instruction now suggested is not in conformity with the present requirements of examining bodies. Its general adoption must therefore depend on their co-operation.

Suggestions for a Course of Elementary Instruction in Physical Science. Drawn up by Professor Armstrong.

Although the Committee is ostensibly charged to report as to methods of teaching *chemistry*, chemistry pure and simple is not what is required in schools generally, and therefore the Committee must be prepared to take into consideration and make recommendations as to a course of instruction preliminary to the natural science course proper, which in their opinion affords the most suitable and efficient preparation for later natural science studies.

After the most careful consideration of the question during at least ten years past, and after long holding the opinion that chemistry, as usually understood, is not the most suitable science subject for school purposes, I am now of opinion that a course which is mainly chemical is not only the best, but also the only one possible if we are to secure all the objects aimed at in introducing science teaching in schools. Those objects are essentially: to train boys and girls to use their brains; to train their intelligence; to make them observing and reasoning beings, accurate observers and accurate thinkers; to teach them to experiment, and that, too, always with an object—more frequently than not with what may be termed a logical object—not for mere descriptive purposes; to gradually inculcate the power of "doing," on which Charles Kingsley has laid so much stress, and which undoubtedly is the main factor of success in life. It can scarcely be gainsaid that through chemistry more than through any other branch of natural science it is possible to give precisely that kind of "practical" training so requisite at the present day, because the student is able to ascertain *by experiment* what are the exact facts, and thus to arrive independently at an explanation, whereas in the case of other sciences, more often than not the explanation of necessity has to be given by the teacher.

Chemistry as usually taught loses greatly in educational value because pupils are told, more often than not, that "so and so is the case," instead of being taught *how it has been found out* that such is the case; indeed, that which has to be proved is usually taken for granted. Practical chemistry has hitherto, as a rule, been interpreted to mean the preparation of a few gases, &c., and the analysis of simple salts. Much useful information may be and is occasionally imparted during the performance of exercises of this kind, but the tendency undoubtedly is for analysis to degenerate into a mechanical drill, and, looking at the question from the practical point of view, and, considering what is the general outcome of such teaching, probably we are bound to agree that the results thus far obtained are usually unsatisfactory. The difficulty, however, is to devise a course sufficiently simple both in conception and when carried into practice, the cost of which is not too great; but with respect to this item of cost the Committee has to make clear to parents and teachers the claim of natural science to a fair and proportionate share of the total expenditure, which certainly has never yet been granted to it. By the introduction of such studies into the school course a set of faculties are trained which it is all-important to develop, but which hitherto have been allowed to remain dormant, if not to atrophy, through neglect, and which, it is admitted by all competent authorities, cannot possibly be developed by any amount of attention paid to literary and mathematical studies. It is often not sufficiently clearly stated or understood that the advocates of natural science studies have no desire to displace any of the traditional subjects from the school course, and that all that they ask for is a fair share of the child's time, attention, and brains—a share proportionate to the effect which such studies can demonstrably produce in developing the mental faculties of the individual: that, in fact, natural science claims to co-operate and in no sense puts in an appearance as a rival.

Stage I.—*Lessons on Common and Familiar Objects.*

The first stage of instruction must be one of simple object lessons, but these should have an intimate relation to the child's surroundings, and should be made the pegs on which to hang many a tale. Probably the most satisfactory and practical mode of commencing is to get children to draw up lists of familiar and common objects under various heads, such as—

Natural objects.

Things used in building construction.

Things from which household furniture is made or which are in daily use.

Things used as clothing.

Food materials.

The children should be induced to describe these from observation as far as possible; to classify them according to their origin into mineral and animal and vegetable or organic; and occasion should be taken at this stage to give, by means of reading lessons and demonstrations, as much information as possible about the different things, their origin, how made, and their uses. It is obvious that in this way a great deal of geography and natural history (*Naturkunde*) might be taught in an attractive manner. Geikie's "Science Primer on Physical Geography" is the type of book which may be worked through with great advantage at this stage.

Stage II.—*Lessons in Measurement.*

This stage should be entered upon as soon as children have learnt the simple rules of arithmetic, and are able to add, subtract, multiply, and divide—and to use decimals.

Lineal measurements may be first made, using both an an English foot-rule with the inch subdivided in various ways, and a metric rule subdivided into millimetres. In this way the relation of the two scales is soon insensibly learnt.

Measurements of rectangular figures and the calculation of their areas may then be made.

After this the use of the balance may be taught, and the relation between the French and English systems may be learnt by weighing the same objects with the two kinds of weights. Use may then be made of the balance in determining the areas of irregular figures by cutting out rectangular and irregular figures from the same cardboard or thin sheet metal, and weighing these, &c.

Solid figures are next studied: a number of cubes made from the same wood having been measured, their volumes are then calculated, and the results thus obtained are compared with those which are obtained on weighing the cubes. The dimensions and weights of cubes made from different woods or other materials are then ascertained, and thus it is observed that different materials differ in *density*. The study of the *relative density* of things generally is then entered upon. The ordinary method is easily learnt and used by children, a suitable bottle being provided by filing a nick down the stopper of a common two-ounce narrow mouth bottle; it may then be shown that the same results are obtained by the hydrostatic method of weighing in air and water, and it is not diffi-

cult to lead children to understand this latter method after they have determined the heights of balancing columns of liquids, such as turpentine, water, and saturated brine, of which they have previously ascertained the relative density. These hydrostatic experiments are of value at a later stage in considering the effects of atmospheric pressure.

By determining the dimensions of a cube and the weight of the water which it will displace, an opportunity is afforded to point out that if the results are expressed in cubic centimetres and grammes respectively there is a practical agreement between the numbers, and hence, to explain the origin of the metric system of weights and the relationship between its measures and weights; the irrationality of the English system may then be explained.

The relative densities of a large number of common substances having been ascertained, the results may be tabulated and then the value of the data as criteria may be insisted on; as an illustration of their value, quartz, flint, sand, and gravel pebbles may be selected. The children having determined their relative densities, the agreement between the results may be pointed out and the identity of the material explained. By drawing perpendiculars corresponding in height to the densities of various substances, a graphic representation is obtained which serves to bring out the value of the graphic method of representation.

A very valuable exercise to introduce at this stage is based on the well-known fact that in certain conditions of the atmosphere things appear moist: a muslin bag full of seaweed may be hung up under cover but freely exposed, and may then be weighed daily at a given time; simultaneously the state of the weather, direction of the wind, the height of the barometer, and the wet and dry bulb thermometer may be noted; on tabulating the results, and especially if the graphic method be employed, the variations and their relationship will be noticeable.

The thermometer, having thus become a familiar instrument, may be used to examine melting ice and boiling water; the construction of both the Centigrade and Fahrenheit thermometer may then be explained, and the effect of heat on bodies made clear. The density of ice and of water at various temperatures may then be determined, a Sprengel tube—which is easily made—being used for warm water; the bursting of pipes in winter, the formation of ice on the surface of water, &c., may then be explained. Afterwards, simple determinations of the heat capacity of a few metals, &c., and of the latent heat of water and steam, may be made in accordance with the directions given in a book such as Worthington's "Practical Physics."

Stage III.—*Studies of the Effect of Heat on Things Generally; of their Behaviour when Burnt.*

As it is a matter of common observation that heat alters most things, the effects of heat on things generally should be studied; in the first instance qualitatively, but subsequently, and as early as possible, quantitatively. Bits of the common metals may be heated in the bowl of an ordinary clay pipe plunged into a clear space in any ordinary fire, or in such a pipe or a small iron spoon over a gas-flame. The difference in fusibility is at once apparent, and in the case of metals like iron and copper it is noticeable that although fusion does not take place, a superficial change is produced; the gradual formation of a skin on the surface of fused lead and tin is also easily perceived. Observations like this become of great importance at a later stage, and indeed serve to suggest further experiments: this is a point of special importance, and from the beginning of this stage great attention should be paid to inculcating habits of correct observation; the effect should first be recorded by the pupil, the notes should then be discussed and their incompleteness pointed out, and they should afterwards be re-written. The fusibility of substances which are not affected when heated in the tobacco-pipe may be tested by heating them with a Fletcher gas blowpipe on charcoal, and by heating little bits of wire or foil in such a flame it is easy for children to discover the changes which metals undergo when burnt, especially in cases such as that of zinc or copper or iron.

The further study of the effect of heat should be quantitative, and may well commence with water. It being observed that water disappears on heating, water may be put into a clock-glass or glass dish placed on a water-bath (small saucepan); it evaporates and it is then observed that something is left. A known quantity of water by weight or volume is therefore evaporated and the residue weighed. This leads to the discovery that water contains something in solution. The question then naturally arises, What about the water that escapes? so the steam is condensed and the distilled water evaporated. The conception of pure water is thus acquired. An experiment or two on dissolution—using salt and sugar—may then be introduced, a water oven or even an air oven (a small Fletcher oven) kept at a known temperature being used, and the residue dried until the weight is constant. Rain and sea water may next be examined; the results afford an opportunity of explaining the origin of rain and of accounting for the presence of such a large quantity of dissolved matter in sea water. Then the various common food materials may be systematically studied, commencing with milk; they should first be dried in the oven, then carbonised and the amount of char determined, then burnt and the percentage of ashes determined. A small platinum dish, 15 to 20 grms. in weight, is required for these experiments, and a gas muffle furnace is of the greatest use in burning the char and in oxidising metals. In addition to the discipline afforded by such experiments a large amount of valuable information is acquired, and the all-important fact is established that food materials generally are combustible substances. Afterwards mineral substances are examined in a similar manner, such as sand, clay, chalk, sulphur, &c., and then metals, such as lead, copper, tin, and iron may be studied; their increase in weight is in striking contrast to the inalterability of substances like sand and salt, and the destruction of vegetable and animal substances. Chalk, from which lime is made by burning, is found to occupy a middle position, losing somewhat in weight when strongly heated. The exceptional behaviour of coal among mineral substances, and of salt among food materials, is shown to be capable of explanation, inasmuch as coal is in reality a vegetable and salt a mineral substance; but sulphur remains an instance of exceptional behaviour requiring explanation. It is not exceptional in being combustible as metals like magnesium and zinc are combustible, but in affording no visible product. The smell of burning sulphur, however, serves to suggest that perhaps after all there is a something formed which is an invisible substance possessed of an odour, and then follows quite naturally the suggestion that perhaps in other cases where no visible or perceptible product is obtained—as on burning charcoal, for instance—there may nevertheless be a product. Whereas, therefore, in Stage I. the pupil will have learnt to appreciate the existence of a great variety of substances, and will have gained the power of describing their outward appearance more or less fully; and in Stage II. having learnt how to measure and weigh, will acquire the habit of determining by measurement certain properties of substances, and will thus be in a position to express in exact terms the kind of differences observed; in Stage III. the pupil will be led to see that profound changes take place on burning substances, and that these changes involve something more than the destruction of the things burnt. The foundation is thus laid for the study of change, *i.e.*, chemical studies proper.

Stage IV.—*The Problem Stage.*

Many of the changes observed in the course of the experiments made in Stage III. might be examined and

their nature determined, but the best to take first is a very familiar case, that of the rusting of iron.

Problem I. *To Determine what Happens when Iron Rusts.*—The pupil *must* be led in the first instance to realise that a problem is to be solved and that the detective's method must be adopted and a *clue* sought for. It is a familiar observation that iron rusts, especially when wet; what happens to the iron, why does it rust, is the iron alone concerned in the change? No information can be gained by looking at it—perhaps the balance which has brought to light so much in Stage III. may be of service, so the iron is allowed to rust in such a manner that any change in weight can be observed. A few grms. of iron-filing or borings are put on to a weighed saucer or clock-glass along with a bit of stiff brass or copper wire to be used as a stirrer; the iron is weighed, then moistened and exposed under a paper cover to keep off dust, preferably in a warm place; it is kept moist and occasionally stirred. After a few days it is dried in the oven and then weighed. The weight is greater. *Something from somewhere has been added to the iron.* Thus the clue is gained. Where did this something come from? The fact that when a tumbler, for instance, is plunged mouth downwards into water the water does not enter, and that on gradually tilting the tumbler to one side something escapes—viz., air—at once affords a demonstration of the presence of air in the space around us. The iron rusted in this air, but was kept moist, so it may have taken up the something from either the air or the water. To ascertain whether the air takes part in the rusting, some iron borings are tied up in a bit of muslin and the bag is hung from a wire stand placed in a (jam) pot full of water and a so-called empty (pickle) bottle, which in reality is full of air, is inverted over the iron; in the course of a few hours, as the iron rusts, the water is observed to rise until it occupies about one-fifth of the jar (determined by measuring or weighing the water); the something added to the iron during rusting appears therefore to come from the air, and the all-important fact is thus discovered that the rusting is a change in which not the iron alone, but also the air, is concerned. The experiment is several times repeated, fresh iron being used with the same air and the same iron put in succession into fresh portions of air, but the same result is always obtained: whence it follows that whatever it is in the air which takes part in the rusting, the air as a whole is not active. The changes previously observed to take place when iron, copper, lead, zinc, &c., were heated in air, are then recalled; as the metals were found to increase in weight it would appear probable that in these cases of change also the air was concerned.

These results at once suggest the question, What is air? So much having been learnt by studying the change which iron undergoes in rusting, other changes which happen in air therefore are next studied.

Problem II.—*To Determine the Nature of the Changes which take place on Burning Substances in Air.*—The use of phosphorus is introduced by reference to a match. Phosphorus is then burnt under a bell jar over water and the result noted: the disappearance of some of the air again shows that the air is concerned. The fact that phosphorus smokes when taken out of the water in which it is always kept suggests that some change is going on, so a stick of phosphorus is exposed in air as in the previous experiment with iron; soon one-fifth has disappeared and the phosphorus then ceases to smoke. The *quantitative* similarity of the two results suggests that iron and phosphorus behave alike towards air and *vice versâ*, and serves to confirm the idea that some constituent of the air present only to the extent of about one-fifth is active. But nothing is to be taken for granted, so iron is exposed in the phosphorus-air residue and phosphorus in the iron-air residue: as no change occurs there is no room left for doubt. Recalling the experiments in which various metals were burnt in air in order to determine whether in these cases the same constituent of the air was concerned in the change, air from which the active constituent has been removed by means of phosphorus, is passed through a heated tube containing bits of the metals: no change is observed, so it is evident that as a rule, if not always, one and the same constituent of air is concerned. The experiments with iron and phosphorus, although they show that the air is concerned in the changes which are observed to take place, do not afford any information whether or no the water which is also present is concerned in the change. Phosphorus is therefore burnt in a "Florence" flask closed with a rubber stopper: on removing the stopper under water some water enters, and by measuring this and the amount of water which will fill the flask the same result is obtained as in the previous cases. To be certain whether in this case anything enters or escapes from the flask it is weighed before and after the phosphorus is burnt. There is no change in weight. But does nothing escape? Yes, much heat; whence it follows that heat is not material: that, although some of the air disappears, it is merely because it has become affixed to or absorbed by something else. This has been proved in the case of the rusting iron and the burnt metals. To obtain indisputable evidence in the case of the phosphorus this is burnt in a current of air in a tube loosely filled with asbestos to retain the smoke: the weight is round to increase. The observation that the phosphorus ceases to burn after a time suggests the introduction of a burning taper into the residue left by iron, &c.; it is found to be extinguished. Then a candle and subsequently a gas flame may be burnt in a bell jar full of air over water. Reversed combustion may then be demonstrated in order to fully illustrate the reciprocal character of the phenomena. Thus it is ascertained that in all ordinary cases of combustion are changes in which the air, and not the air as a whole, but a particular constituent, is concerned, and no doubt remains that the same constituent is always active, but active under different conditions; it is realised also that the production of heat is the consequence of the union of the substance burnt with the active substance in air. The experiment of exposing phosphorus in air affords the opportunity of demonstrating the evolution of heat even in a case where no visible combustion occurs, as the phosphorus is always observed to melt. At this stage careful note should be taken of the appearance of the different products of combustion and of a change such as that which occurs when the product from phosphorus is exposed to the air.

(To be continued).

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 9, August 26, 1889.

The Relations of Atmospheric Nitrogen to Vegetable Mould. A Reply to M. Berthelot.—Th. Schlœsing.—M. Berthelot, in invoking the results of MM. Dehérain, Hellriegel, Wilfarth, Breal, and Frank in support of his conclusions, confounds two distinct questions—the fixation of gaseous nitrogen by vegetable mould, and the fixation of gaseous nitrogen by certain vegetable species. The author has merely dealt with the former question, whilst the observations and experiments of the authorities cited concern specially the latter question, and do not solve the former. He maintains his former conclusions, *i.e.*, that he has not succeeded in witnessing the fixation of nitrogen by bare vegetable mould without vegetation, though experimenting under the very same conditions which M. Berthelot has observed.

Action of Water upon Stannic Chloride.—Leo Vignon.—If stannic chloride is mixed with water the result is a solution of stannic oxide in dilute hydrochloric acid. This stannic oxide, which is very unstable, tends to become polymerised. In time the polymerisation reaches a certain state of equilibrium, which is a function of the dilution, the temperature, and the chemical composition of the liquid.

The Action of Phosphates upon the Cultivation of Cereals.—G. Raulin.—It is probable that in agricultural practice we may employ the natural tribasic phosphates containing phosphoric acid in the so-called insoluble state if the former are applied in large proportions varied according to the crops and the nature of the soil for the first years.

No. 10, September 2, 1889.

Researches on the Relations Existing between the Colour of Plants and the Richness of the Soil in Agents of Fertility.—Georges Ville.—The author has studied the colour of the leaves of plants in the time before flowering, in connection with the fertility of the soil. He finds that this colour experiences a decided change if one of the four constituents of his "complete" manure is wanting in the soil. Its intensity increases or decreases; the colour remains green or turns yellow according as the soil is wanting in phosphate, in potassa, or in nitrogen. He has fixed the exact shade by the aid of Chevreul's chromatic circles. In plants which especially require nitrogen the leaves turn yellowish in its absence. For greater precision he compares the colouring-matter extracted and diluted in a constant volume of alcohol. He first removes the erythrophyll (carotine) by treatment with petroleum ether, and then extracts the leaves with absolute alcohol, which takes up all the chlorophyll. The liquids thus obtained are then compared.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xix., No. 12.

The Origin of Bronze and the Sceptre of Pepi I., King of Egypt.—M. Berthelot.—Already noticed.

The Use of Cold in the Preparation of Pharmaceutical Extracts.—L. A. Adrian.—From the *Bulletin Soc. Chim. de Paris.*

MISCELLANEOUS.

Manures and Their Uses.—Dr. A. B. Griffiths's work on this subject has just been published by Messrs. George Bell and Sons.

Guy's Hospital.—The Open Scholarships in Arts have this year been awarded to Mr. William S. Handley, Loughborough Grammar School, and Mr. John Robert Steinhaeuser, Sutton Valence School. The Open Scholarships in Science have been awarded to Mr. John A. Howard, King's College and Guy's Hospital, and to Mr. Arthur H. Leete, University College, Aberystwith.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Manures.—Can any reader refer me to papers treating on chemical manure, shoddy manure especially?—H. Thompson.

Crystalline Metal.—Can any reader tell me if there is any known metal which crystallises from, and is precipitated from, solution as threads three or four inches long, of a golden and rose-red colour with metallic lustre?—Unknown.

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See opinion *Electrical Review*, October 21.

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THE CHEMICAL NEWS.

Vol. LX. No. 1559.

ON THE

DETECTION OF ADULTERATION IN ESSENTIAL OILS.

By ROWLAND WILLIAMS, F.I.C., F.C.S.

Our knowledge of the chemical properties of the majority of the essential oils is comparatively limited, notwithstanding the fact that many chemists have devoted a good deal of time to the investigation of these important substances. The most exhaustive research in connection with this subject of which I can find any record is that by Dr. Gladstone, the results of which are given in three papers published in the *Journal of the Chemical Society* (vol. xvii., p. 1; vol. xxv., p. 1; and vol. xlix., p. 609). In these papers Dr. Gladstone treats more particularly of the optical characters of nearly 60 kinds of essential oils, which he took great precaution to obtain in a perfectly pure condition. He gives the specific gravity, refractive indices, and rotation of the original oils; and, besides these data, he records the boiling-points, dispersion, sensitiveness, and specific refractive energy of certain hydrocarbons prepared therefrom. All three papers are full of useful information, and will well repay careful perusal.

Other valuable papers, dealing with various essential oils, have been published by Alder-Wright, Pattison-Muir, Tilden, Armstrong, Atkinson and Yoshida, Hartley and Huntington, Kingzett, and other chemists.

As most of the methods hitherto described in connection with the examination of essential oils have, as their main object, the qualitative detection of certain impurities and adulterants, *e.g.*, water and alcohol, I have recently investigated the subject from what is, I believe, a novel point of view so far as essential oils are concerned, in order to ascertain whether it is possible by any means not only to detect, but also to estimate, the proportion of such foreign ingredients.

For this purpose I purchased some 60 specimens, representing 26 of the most important essential oils occurring in commerce. It will, of course, be understood that it was necessary these oils should be of undoubted purity, or they would be useless for the object I had in view. I therefore communicated with some of the largest dealers in essential oils, and, having stated the nature of my proposed research, they undertook to supply me with the oils which I required. I may mention that the firms in question were the actual distillers of the majority of the oils, so the purity of most of these can, I think, be relied upon.

Two specimens, at least, of each kind of oil were examined, and in some cases several. In each of these oils I determined the specific gravity at 60° F., potash absorption, iodine absorption, and boiling-point.

With regard to the specific gravity determinations, although the figures from most of my duplicate samples agree fairly well among themselves, they do not, on the whole, correspond very closely with those obtained by Dr. Gladstone in his examination of similar oils.

The percentage of potash absorbed by each oil was ascertained by boiling a weighed quantity of the sample with an excess of seminormal alcoholic potash and titrating back with seminormal acid. Important results were obtained by this method of examination in the case of several of the oils.

The proportion of iodine absorbed by fixed fats and oils has been found so useful a factor in the detection of adulteration in those substances that I determined to estimate the iodine absorption of the essential oils which I was examining. To the best of my knowledge this test has never before been applied to essential oils—at any rate not to a large number of representative samples. The figures which I obtained by this method are in many instances highly instructive, and the boiling-point determinations will also be found to present some interesting features.

In the following table are recorded the results obtained by examining the oils in the manner indicated above:—

It will be seen from the above table that in many cases the two or more specimens of certain of the essential oils which I examined, although obtained from widely different sources, gave very concordant results. This remark applies more especially to the oils of bergamot, caraway, cassia, cedar-wood, cinnamon, citron, citronelle, cloves, lemon, mace, nutmeg, orange, thyme, and verbena.

On the other hand, the figures yielded by several of the oils compare unsatisfactorily with one another. This may possibly be due to actual adulteration of the oils in question, or to the presence of accidental impurities therein, or it may be caused by change in the composition of the oils through oxidation. The tendency of essential oils to become oxidised is well known, and it is probably due to this fact that what may be termed "the acidity expressed in terms of potash" appears so much greater in some of the oils than in others of the same kind—this liability to oxidation being, of course, more characteristic of some essential oils than of others, and depending to a considerable extent upon the mode and duration of storage. I ought, perhaps, to mention that one of my chief objects in undertaking this investigation was to see whether it was possible to discriminate by chemical analysis between the English and foreign varieties of those two highly important oils lavender and peppermint; because, if so, the results would be valuable from a commercial as well as from a scientific point of view. Unfortunately my hopes have not been realised so far as these particular oils are concerned. As a matter of fact, judging from the results which I have obtained, it would seem impossible to distinguish by the methods employed in this investigation between English and foreign oils of lavender, although an experienced person can easily detect an appreciable difference by the sense of smell.

The most striking difference between the two kinds of oil of lavender seems to be that French absorbs a larger quantity of potash than English, but without further investigation this can hardly be regarded as a characteristic feature. Addition of a considerable amount of "spike" oil to the more expensive oils of lavender would probably be indicated by a decrease in the boiling-point and in the percentage of potash absorbed by the mixture.

With regard to oil of peppermint, very little difference exists between the specific gravity, potash absorption, and boiling-point of the three varieties which I examined. There is, however, rather a wide divergence between the iodine absorptions, even between those of the same variety of peppermint oil. I am unable to offer any satisfactory explanation of these discrepancies, but there is no doubt about the accuracy of the figures, duplicate determinations being made in the case of all the oils.

The results obtained from the oils of lemon, citron, and orange are remarkably concordant and very interesting, both as regards pointing to the similarity of their respective constitutions and also as showing that adulteration of these valuable oils could be detected by chemical analysis.

It will be observed that oil of bergamot is the most acid of all the oils examined. This acidity I have found to be partly due to the presence of citric acid.

In speaking of the oils of cinnamon and cassia, Allen says ("Commercial Organic Analysis," vol. iii., p. 45):—"No sharp distinction exists between the two oils, or one which would enable one to be detected with certainty in presence of the other." This statement is contrary to my experience. There are, indeed, several striking points of

Name of Oil.	Specific gravity at 60° F.	Potash absorbed. Per cent.	Iodine absorbed. Per cent.	Boiling-point in ° F.
Aniseed—				
No. 1	0·976	0·25	274·44	434
No. 2	0·984	0·38	185·92	442
Bergamot—				
No. 1	0·879	11·43	247·90	374
No. 2	0·878	8·78	283·71	370
Cajeput—				
No. 1	0·918	0·35	70·85	490
No. 2	0·889	0·41	151·00	486
Caraway—				
No. 1	0·910	0·53	258·26	379
No. 2	0·913	0·35	263·22	388
Cassia—				
No. 1	1·061	10·17	75·06	490
No. 2	1·051	9·62	71·71	486
Cedar-wood—				
No. 1	0·952	0·92	78·51	518
No. 2	0·963	0·92	74·77	520
Cinnamon—				
No. 1	1·031	5·13	128·14	464
No. 2	1·021	4·91	105·05	466
Citron—				
No. 1	0·855	0·67	359·66	348
No. 2	0·871	1·90	320·04	346
No. 3	0·855	1·31	353 94	348
Citronelle—				
No. 1	0·893	3·35	186·30	416
No. 2	0·897	3·43	191·26	426
Cloves—				
No. 1	1·046	2·48	179·83	476
No. 2	1·041	2·35	155·46	478
Eucalyptus—				
No. 1	0·910	0·52	61·68	348
No. 2	0·910	0·36	106·46	350
No. 3	0·888	0·35	110·65	350
Juniper—				
No. 1	0·872	1·12	273·55	340
No. 2	0·878	0·84	236·09	344
No. 3	0·881	0·70	250·06	360
Lavender, English—				
No. 1	0·883	3·70	230·38	378
No. 2	0 887	3·17	248·59	374
No. 3	0·878	0·52	232·92	378
(Samples Nos. 1 and 2 are from Mitcham, Surrey, and No. 3 from Hitchin, Hertfordshire).				
Lavender, French—				
No. 1	0·893	4·85	198·65	378
No. 2	0·881	9·20	237·21	376
No. 3	—	4·90	199·18	—
Lavender, "Spike"—				
No. 1	0·873	1·99	287·90	330
No. 2	0·904	0·74	207·01	340
Lemon—				
No. 1	0·856	1·49	322·96	349
No. 2	0·858	1·41	320·16	352
Lemon-grass—				
No. 1	0·897	2 25	223·24	432
No. 2	0·898	2·01	271·52	432
Mace—				
No. 1	0·886	0·85	220·85	346
No. 2	0·900	0·67	224·02	346
Nutmeg—				
No. 1	0·883	0·35	201·93	340
No. 2	0·898	0·19	206 24	342
Orange—				
No. 1	0·849	0·39	347·67	348
No. 2	0·853	0·38	341·75	351
Pennyroyal—				
No. 1	0·925	1·46	85·94	420
No. 2	0 939	4·62	78·58	418
Peppermint, Mitcham—				
No. 1	0·903	1·83	36·85	404
No. 2	0·908	1·97	46·37	407
Peppermint, American—				
No. 1	0·911	4·37	71·70	402
No. 2	0·904	2·71	53·09	400
Peppermint, Japanese—				
No. 1	0·900	2·29	56·06	400
No. 2	0·896	2·22	37·08	398
Rosemary—				
No. 1	0·894	0·78	161·67	335
No. 2	0·912	0·88	142·36	333
Rue—				
No. 1	0·860	0·56	192·02	338
No. 2	0·871	0·29	121·32	384
Sage—				
No. 1	0·961	7·09	49·70	360
No. 2	0·918	1·58	117·14	364
Sassafras—				
No. 1	1·056	0·33	162·68	430
No. 2	1·079	0·28	151·01	448
Thyme (red)—				
No. 1	0·892	1·91	181·48	338
No. 2	0·893	1·09	168·40	356
Verbena—				
No. 1	0·896	1·20	267·83	430
No. 2	0·895	1·37	247·81	430

distinction between the two oils, and, judging from the results of my experiments, it is evident that here, again, chemical analysis would be useful not only in detecting, but also in approximately estimating the proportion of adulteration in the case of the admixture of oil of cassia or other inferior oils with the more expensive oil of cinnamon. When it is remembered that the value of good oil of cinnamon is at least a dozen times that of oil of cassia the importance of this fact can hardly be over-estimated.

The greatest discrepancies of all occur between the two specimens of sage oil, and it is evident that there must be a considerable difference between their respective constitutions. According to Pattison-Muir (*Journal of the Chemical Society*, vol. xxxvii., p. 680) the composition of sage oil varies with the age of the sample. Soon after distillation comparatively small quantities of salviol, camphor, and cedrene are present, but as the oil increases in age the proportion of the two former bodies becomes larger and the $C_{10}H_{16}$ hydrocarbons decrease, while a hydrocarbon or hydrocarbons of the formula $C_{15}H_{24}$ is produced. This may, perhaps, account for the peculiar results which I obtained from the two specimens of sage oil which I examined.

When the costly nature of many of the essential oils is taken into consideration it is only to be expected that a good deal of adulteration will take place in connection with these substances. I understand that one of the cheapest, if not the cheapest, of the essential oils—citronelle—is largely sophisticated with kerosine oil, and the adulteration is said to be on the increase. What, then, must be the case with some of the more expensive oils, the price of which is enormous when compared with that of citronelle? There can be no doubt that the difficulty, and indeed, frequently, the impossibility, which has hitherto existed of detecting the presence of adulterants in essential oils by means of chemical analysis has led to an increase in this form of fraud. It is, therefore, gratifying to know that, by the use of the methods of examination which I have indicated above, the purity or otherwise of many essential oils can be determined with certainty.

Before concluding I should like to express my thanks to my assistants, Messrs. H. Winstanley and C. Boothby, for their valuable aid in the course of this investigation.

Laboratory and Assay Office,
28, Pall Mall, Manchester,
September 14, 1889.

ANALYTICAL STUDIES ON PHOSPHODODEKAMOLYBDIC ACID, THE CONDITIONS OF ITS FORMATION, AND ITS SEPARATION AS AN AMMONIUM SALT.

By Dr. FRANZ HUNDESHAGEN.

(Continued from p. 170).

The Formation of Triammoniumphosphododekamolybdate from its Elements present in Neutral Solutions under the Influence of Nitric Acid.

The author used in each experiment 0·010 grm. P_2O_5 and 0·243 grm. MoO_3, both bodies being consequently in the molecular proportion—

$$P_2O_5 : 24MoO_3.$$

The concentration of the nitric acid was taken, so that 0·04437 grm. NO_3H were present in the c.c., which quantity represented 10 mols. in reference to the P_2O_5 present, or 5 mols. if referred to the mol. of the phosphomolybdate to be precipitated The number of the c.c. nitric acid consumed multiplied by 5 showed how many mols. nitric acid were introduced every moment to one mol. ammoniumphosphomolybdate.

The mixture of the measured solutions of molybdate and phosphate was coloured with a little alkaline phenolphthalein, and was then accurately neutralised with dilute nitric acid. After adding a few grms. of neutral ammonium nitrate the whole was made up to 50 c.c. and, whilst constantly stirring, the standard nitric acid was added by drops from a burette and, with occasional interruptions (the solution being heated more and more, and ultimately, when there was no longer any fear of a loss of ammonia, nearly to a boil), until a distinct and permanent yellow colour appeared.

Here there were consumed 2·95—3·05 c.c. acid, or a mean of 3·00 c.c. = 15 mols.

Up to 3·30 the colour became constantly brighter, but the local precipitates disappeared again, all save a permanent unimportant turbidity.

From 3·35—3·45 c.c. (=17 mols.) every drop occasioned a strong permanent precipitate up to about 4·50 to 4·60 c.c. = 23 mols. NO_3H, when the liquid began to grow clear.

Up to 5·10—5·20 c.c. only slight pale yellow precipitations were perceptible; beyond this limit (about 26 mols.) the precipitation of the ammonium phosphomolybdate was completed.

The following considerations will assist us in the interpretation of the three main phases of this reaction:—

The colourless liquid which represents the end of the first phase has exactly the properties of the solution we obtain on treating ammonium phosphomolybdate with ammonia, repeatedly evaporating off the liquid, renewing the water until no more ammonia is given off, and redissolving the colourless residue in water. This residue, which Hehner, *Zcitschrift*, xx., p. 292, recommends as a fit form for weighing, contains, according to him, when dry $\frac{2}{3}\frac{1}{8}\cdot\frac{5}{5}$ = 3·509 per cent P_2O_5.

It is doubtless a mixture of hexammonium diphosphopentamolybdate and hexammonium heptamolybdate.

Fifteen mols. were found experimentally as the quantity of acid which is required to produce an incipient yellowness.

The second phase, between 15 and 17, is characterised by an increasing yellowness without permanent separation, and may be explained by the assumption of the formation of a soluble yellow intermediate product of the colourless soluble and of the yellow insoluble phosphomolybdate.

In the third phase, in presence of 6 more mols. NO_3H, the 7 mols. MoO_3 contained in heptamolybdate unite with the pentamolybdate to form phosphododekamolybdate.

The ultimate extension of the reaction to 23—26 mols. must be due to the two equivalents of nitric acid, which, as we are justified in assuming, form with the phosphomolybdate an unstable chemical combination, and to the small excess of nitric acid which promotes the completion of the separation.

It is to be noted that an excess of either component of phosphododekamolybdic acid in its original neutral solution involves an increased consumption of nitric acid, so that for every 6 mols. of $MoO_4(NH_4)_2$ present in excess there are required 11 mols. NO_3H, and for each mol. $PO_4H(NH_4)_2$ about 2 mols. NO_3H, for the separation of the phosphomolybdate more than if the substances had been mixed in the exact proportion—

$$P_2O_5 : 24MoO_3.$$

As for the first case 11 mols. of NO_3H are exactly the quantity which would convert 6 mols. $MoO_4(NH_4)_2$ into an acid molybdate containing $1NH_4$ to MoO_3. In the second case, 2 mols. NO_3H would be more than sufficient to convert the excessive hydrophosphate into dihydrophosphate.

These facts compel us to assume that the formation of the phosphododekamolybdate depends on the presence of monammonium hexamolybdate on the one hand, and dihydrophosphate on the other, and on a condensation of two mols. of the former body with one mol. of the latter, two mols. of water being eliminated. The yellow phosphododekamolybdic acid should therefore be a phosphodihexamolybdic acid.

Influence of an Excess of Nitric Acid upon the Formation and Dissociation of Phosphododekamolybdic Acid, and the Quantity of Molybdic Acid Requisite for its Separation.

1. The phenomena of the dissociation of phosphomolybdic acid have been studied in the following manner:—

Mixtures of 0·010 grm. P_2O_5 and 0·243 grm. MoO_3 were again employed. To prevent an undesirable increase of the volume the nitric acid was taken at ten times the strength, as in the former experiments, so that with each c.c. of acid 50 mols. of nitric acid were introduced to the mol. of the phosphomolybdate present in its elements. From obvious reasons the nitric acid could not be added to the complete mixture of phosphate and molybdate. There was first prepared a mixture of neutral molybdate with ammonium nitrate, the required quantity of nitric acid was added, the measured dose of phosphate solution run in with agitation, and in order to preserve in all cases the same molecular concentration for P_2O_5 and MoO_3 the liquid was made up to 60 c.c. To prevent any disturbing loss of acid by evaporation a condenser was connected with the flask during heating.

The solutions with slight excess of acid deposited the yellow precipitate in a few moments or minutes; in those richer in acid the precipitation was slower and less perfect, and where the excess of acid was very great it did not occur at all.

As soon, in each case, as the deposition had reached its maximum, indicated by the phenomenon that after removing the yellow matter from one part of the side of the glass subsequent rubbing with the stirring rod and prolonged heating did not lead to its re-formation, the hot liquid was filtered, the precipitate was washed with dilute nitric acid, containing ammonium nitrate, and the filtrate with the washings was saturated with ammonia down to the most desirable point of acidity.

The occurrence of a faint yellow colour without the subsequent settlement of a precipitate indicates traces of phosphoric acid and molybdic acid, which are contained in the filtrate in consequence of incipient dissociation. The dissociation, increasing with the acidity of the solution is indicated by the increase of the precipitates produced in the filtrate on neutralising the acid. They were brought upon the filter, and weighed in a manner which will be indicated below.

From the point when the separation of the phosphomolybdate from the neutral mixture by means of nitric acid is complete, *i.e.*, 26 mols. up to about 80 mols. (excess = 54 mols.) a dissociation could not be shown. The filtrate from a precipitate thrown down from a solution with 90 mols. became faintly yellow on neutralising the excess of acid. With 100 mols. (excess = 74) the dissociation was more perceptible; the filtrate, after partial neutralisation and concentration, gave traces of a precipitate. From this point the dissociation increased continuously and rapidly, and 2000 mols. nitric acid prevented the precipitation completely; the liquid was colourless, but turned yellow on the addition of a little ammonia, depositing at the same time a little phosphomolybdate. The limit of total dissociation was, therefore, not far overstepped, and would probably fall at about 1900 mols.

In a parallel experiment to determine what quantities of molybdic acid were needed at different degrees of acidity for the complete precipitation of the phosphoric acid, it appeared that the excesses going beyond the normal standard of 24 mols. MoO_3 (to 1 mol. P_2O_5) were almost exactly equal to the quantities of molybdic acid which, in the previous experiment, remained in solution in consequence of dissociation.

The measured volumes of the phosphate solution, acidified with varying quantities of nitric acid, and with the precautions laid down in Section 7, were mixed with a solution containing, per c.c., 0·010 grm. of free molybdic acid until the last drops no longer occasioned precipitation. The precipitates were heated with a further small excess of molybdic acid, washed, and weighed.

(To be continued).

THE MANUFACTURE OF PRUSSIATE OF POTASH.*

By J. B. READMAN, D.Sc., F.R.S.E.

THE first portion of this paper refers to the present condition of this manufacture, describing the present process as very wasteful and imperfect, and shows that very little attention has of late years been devoted to improving the process, which has remained stationary for nearly half a century.

A general sketch of the process now employed in manufacturing prussiate is next given. Then follows a brief notice of the history of prussiate since its discovery last century, and of the processes that have been proposed or patented to improve the manufacture, and lastly, full details of a series of experiments made by the author to produce prussiate by the action of ammonia gas upon red-hot wood charcoal which had been previously saturated with carbonate of potash.

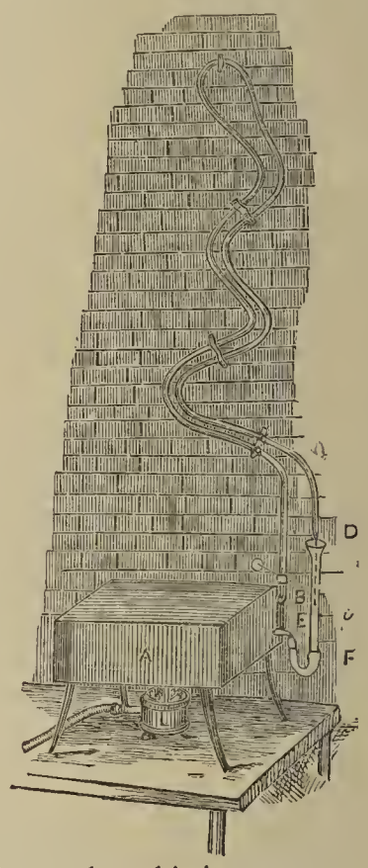
* Read before the British Association, Section B, Newcastle Meeting.

A CONSTANT WATER-BATH.

By Dr. BENNETT F. DAVENPORT.

A DESCRIPTION of this apparatus will be found in the *Pharmaceutische Rundschau* for March, 1887, and in the *Proceedings of the American Pharmaceutical Association* for 1887. It has proven so satisfactory that I think it worth while to repeat the description here for the information of chemists. I have kept my bath boiling day and night seven days in the week, and have added water to it but five times in as many years.

It consists of the square box, A, supported over a Fletcher's solid-flame burner. The top of the box, 15 × 15·5 inches, is formed by a brass plate, ⅛ inch thick, which thus is stiff enough to support a considerable weight without yielding, the sides and bottom being sheet-copper. From the point B projects a ½ inch brass tube, B C, which turns up at a right angle. At E is a stop-cock, which is connected by a thick rubber tube with the glass tube, D F, which is fastened against the adjoining wall. Connected with C by a rubber joint is a ½-inch block-tin tube of 20 feet length, which extends up the wall in the manner shown to the highest point, T, and thence returns and ends just over the slightly funnel-shaped top of the glass tube at D. The bath being filled with water to just the level B *b*, may be kept constant by boiling for many days without appreciable loss of water,



the steam being condensed in its passage up, or if uncondensed before it reaches the point T, in its passage down the block-tin tube. In flat-bottomed platinum or porcelain capsules evaporation goes on very rapidly when placed on top of this water-bath. The whole surface of the bath is nickel plated.—*The Journal of Analytical Chemistry*, Vol. iii., Part 3.

CLASSIFICATION OF THE ATOMIC WEIGHTS IN TWO ASCENDING SERIES, CORRESPONDING TO THE GROUPS OF ARTIADS AND PERISSADS.*

By W. R. LIVERMORE, Major of Engineers, U.S. Army.

(Concluded fom p. 166).

TABLE III. shows the deviations, arranged in the groups and series of the periodic law; the lower division shows the electro-chemical numbers in the same form.

Neglecting insignificant deviations, we find the positive results, or those where the atomic weight is slightly in excess of the serial number, either near the extremes of the electric series, in elements of maximum atomic volume, &c., or in the very centre of this series. The negative results occur half-way between the centre and the extremes. Of the perissads, 1, 2,—31, 32,—57, 59, are positive, and 17, 18, 19, 21,—44, 47, 54, 55, are negative; of the artiads, 7,—46, 51, 53, are positive, and 8, 14, 21, 23, 28, are negative.

* A Paper presented to the American Academy of Arts and Sciences, April 10, 1889.

In the periodic arrangement the first and second groups show positive deviations in the high series of this arrangement; the third, fourth, and fifth, negative in the high series; the sixth, positive in the high series; and the seventh, positive in two terms, and insignificant in two. The seventh and eighth groups are negative in the third series. The deviation of *Zn* is not included in these calculations, nor is the cause of its deviation yet apparent. Perhaps the perissads of the second group are formed from an artiad nucleus, and the artiads of the second group from a perissad nucleus, thus: * 65, 70, 75, 80, &c., and 63 * 71, 75, 79, &c. The last line shows the algebraic mean of the deviations in each group, which, as might be expected, corresponds nearly to the relative atomic volumes.

To do justice to the bearing of these results on the physical question of the ultimate nature of "atoms" would involve a mathematical discussion too prolonged for this paper; but the subject cannot be completed without a brief statement of its relation to well-known systems and theories of chemistry. A few extracts will serve as a basis to show what the perissad law is intended to contribute to the solution of the all-important problem.

In 1854, in a paper read before the American Academy on "The Numerical Relation between the Atomic Weights," Professor Cooke announced the character of the problem as follows:—

"Numerical relations between the atomic weights of the chemical elements have been very frequently noticed by chemists. One of the fullest expositions of these relations was that given by M. Dumas, of Paris, before the British Association for the Advancement of Science, at the meeting of 1851. This distinguished chemist at that time pointed out the fact that many of the elements might be grouped in triads, in which the atomic weight of one was the arithmetical mean of those of the other two. Thus the atomic weight of bromine is the mean between those of chlorine and iodine; that of selenium is the mean between those of sulphur and tellurium; and that of sodium, the mean between those of lithium and potassium.

"M. Dumas also spoke of the remarkable analogies between the properties of the members of these triads, comparing them with similar analogies observed in organic chemistry, and drew, as is well known, from these facts arguments to support the hypothesis of the compound nature of many of the now received elements. Similar views to those of Dumas have been advanced by other chemists.

"The doctrine of triads is, however, as I hope to be able to show in the present memoir, a partial view of this subject, since these triads are only parts of series similar in all respects to the series of homologues of organic chemistry, in which the differences between the atomic weights of the members is a multiple of some whole number. All the elements may be classified into six series, in each of which this number is different, and may be said to characterise its series. In the first it is 9, in the second 8, in the third 6, in the fourth 5, in the fifth 4, and in the last 3." (See Table IV).

The paper speaks of the properties of the elements which are functions of the atomic weights, and says that it does not seem bold theorising to suppose that the atoms of the members of the same series are formed of a common nucleus, to which has been added one or more groups of atoms, or perhaps one or more single atoms, to which the corresponding element has not been discovered.

Referring to this subject in 1857,* M. Dumas said:—"I have often tried, as Mr. Josiah Cooke has on his part, to compare them, to combine them, and to discuss them, with the hope of drawing some conclusion from them with certainty, but I have been unable to draw from them anything but doubt. The formula deduced from the above simple progression" $(a+n\,d)$ "would not account for the generation of simple bodies, as Cooke had supposed; but organic radicles are not always formed by addition, they are also produced by substitution, as we see in the compound ammoniums." Dumas proposed to substitute a formula like $n\ a+n'\,d+n''\,d'$; a being the nucleus, d and d' the common differences, and n, n', n'' whole numbers. Table IV. shows the series of Cooke and Dumas.

Following in their footsteps, Professor Newlands extended their principles to include newly discovered elements. Employing Cannizzaro's atomic weights instead of those of the old system, and collating his own results and all discovered up to 1864, he arranged the groups in horizontal lines instead of vertical columns, and then discovered the "Law of Octaves," as shown in Table IV. The coincidence of the ordinal numbers led him, in 1865, to express the following opinion:—"I will endeavour to show that all the numerical relations among the equivalents pointed out by M. Dumas and others, including the well-known triads, are merely arithmetical results flowing from the existence of the 'law of octaves,' taken in connection with the fact of the equivalents forming a series of numbers approaching to the natural order." And in 1866: "The fact that such a simple relation exists now affords a strong presumptive proof that it will always continue to exist, even should hundreds of new elements be discovered. For, although the difference in the numbers of analogous elements might, in that case, be altered from 7, or a multiple of 7, to 8, 9, 10, 20, or any conceivable figure, the existence of a simple relation among the number of analogous elements would be none the less evident."* The law of regular increase, however, points to a relationship far more significant than the identity of their ordinal numbers.

Working independently of Newlands, Mendeleeff discovered the periodic law in 1869. It has offered a grand incentive to new discoveries and received well-merited recognition throughout the world. The extracts from Wurtz and Meyer, at the beginning of this paper, show what it left to be desired.

A paper by Rev. Dr. Haughton, and an abstract of one by Mr. Stoney, have recently appeared in the CHEMICAL NEWS. Each gives a clear enunciation of the nature of the problem. Dr. Haughton discovers some of the regular intervals noticed here. Unfortunately, the paper of Stoney, on "The Logarithmic Law of Atomic Weights,"† is so abridged that it is hard to determine how his results may compare with those herein discussed. The abstract states that, in plotting the atomic volumes as ordinates of a diagram, the effort to extract information from the resulting curves was a failure; in plotting their cube roots, however, he found a logarithmic curve, with perturbations which showed a distinct law of increase for perissads and artiads. The abstract was not discovered until most of this paper was written, and, from its indefinite statements, it would require much time to construct the curves and divine the inferences.

At the close of his paper of 1854, Professor Cooke said:—"To my conceptions chemistry will then have become a perfect science, when all substances have been classed in series of homologues, and when we can make a table which shall contain, not only every known substance, but also every possible one, and when by means of a few general formulæ we shall be able to express all the properties of matter, so that when the series of a substance and its place in the series are given we shall be able to calculate, nay predict, its properties with absolute certainty. . . . Then the dreams of the ancient alchemist will be realised, for the problem of the transmutation of metals will have been theoretically, if not practically, solved."

* *Comptes Rendus*, 1857, p. 709.

* The "Periodic Law," p. 20.

† CHEMICAL NEWS, vol. lvii., p. 163.

Table III.—*Deviations.*

Grm. Ser.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	−0·03	?	−0·03	0·00	?	−0·01	−0·03	
2	−0·02	−0·02	−0·00	+0·02	−0·08	+0·01	+0·32	
3	−0·02	−0·08	?	0·00	+0·05	+0·19	(−0·26)	−0·11
4	+0·06	?	−0·30	?	−0·06	+0·03	+0·01	
5	+0·64	+0·28	+0·01	−0·80	−0·30	+0·47		+0·02
6	+0·08	+0·03	−0·36	−0·42	−0·14	+0·31	+0·41	
7	+0·25	+0·02	−0·18	?	−0·05			
	+0·14	+0·05	−0·14	−0·25	−0·09	+0·17	+0·18	−0·05

Electro-chemical Order.

1	5	?	49	48	?	63	60	
2	4	9	13	42	55	62	59	
3	3	8	?	43	52	53	(19)	21
4	31	20	?	?	54	56	58	
5	2	7	11	14	44	51		34
6	32	24	27	28	47	46	57	
7	1	6	18	16	17			

Table IV.

Cooke, 1854.

Ser.	III.		IV.	V.	VI.	VIII.	IX.	IV.
Gr.	3.	2. 1.	3, 2. 1.					2. 1. 3.
	H	Ca Mg	Al Ti	C	O	O	O	Al Ti Cu
	Li	Sr Zn	Cr Pd	B	N	S	F	Cr Pd Hg
	Na	Ba Cd	Mn Su	Si	P	Se	Cy	Mn Sn
	K	Pb	Fe Pt		As	Mo	Cl	Fe Pt
	Ag		Co Ir		Sb	Te	Br	Co Ir
			Ni Os		Bi	V	I	Ni Os
			U Au			W		U Au
			Cu			Ta		
			Hg					
	Cu Mn			Ti	Cr V	As Mn	Cr Mn Os Au	

Dumas, 1857.

Form.	7+*n* 8.	12+*n* 8.	25+*n* 34.	6+*n* 5.	14+*n* 17.	8+*n* 8.	19+*n* 16·5+*n*′ 28.
	L	Mg	Ti	C	N	Cr O	F
	Na	Ca	Sn	B	P	Mo S	Cl
	K	Sr	Ta	Si	As	V Se	Br
		Ba		Zr	Sb	W Te	I
		Pb			Bi		

Mendeleeff, 1869.

Gr. Ser.	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
1	H							
2	Li	Be	B	C	N	O	F	
3	Na	Mg	Al	Si	P	S	Cl	
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe Co Ni Cu
5	(Cu)	Zn	Ga	—	As	Se	Br	
6	Rb	Sr	? Y	Zr	Nb	Mo	—	Ru Rh Pd Ag
7	(Ag)	Cd	In	Sn	Sb	Te	I	
8	Cs	Ba	? Di	? Ce				
9	(—)							
10			? Er	? La	Ta	W		Os Ir Pt Au
11	(Au)	Hg	Ti	Pb	Bi			
12				Th		U		

Newlands, 1865.

No.	No.	No.	No.	No.	No.	No.	No.
H 1	F 8	Cl 15	Co & Ni 22	Br 29	Pd 36	I 42	Pt & Ir 50
Li 2	Na 9	K 16	Cu 23	Rb 30	Ag 37	Cs 44	Tl 53
G 3	Mg 10	Ca 17	Zn 25	Sr 31	Cd 38	Ba & V 45	Pb 54
Bo 4	Al 11	Cr 19	Y 24	Ce & La 33	U 40	Ta 46	Th 56
C 5	Si 12	Ti 18	In 26	Zr 32	Sn 39	W 47	Hg 52
N 6	P 13	Mn 20	As 27	Di & Mo 34	Sb 41	Nb 48	Bi 55
O 7	S 14	Fe 21	Se 28	Ro & Ru 35	Te 43	Au 49	Os 51

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

(Continued from p. 173).

PROBLEM III. *To Separate the Active from the Inactive Constituent of Air.*—It now has become of importance to get this active constituent of the air by itself, and the question arises whether it cannot be separated from one of the metals or other substances with which it has been found to combine. The pupil is therefore told to collect information about the different substances formed by burning metals, &c.—whether they can be obtained in sufficient quantity to work with, &c. Iron rust and iron scale are easily obtainable, and so is copper scale; zinc is burnt to produce zinc-white, which is used as paint; lead is also burnt on a large scale, and in this case it appears that one or other of two substances is formed—litharge at a high temperature, red lead at a lower temperature. This peculiarity of lead suggests the study of the two products in the hope of discovering the clue to a method. Weighed quantities of the litharge and red lead are heated; it is observed that only the latter changes in appearance and that it loses weight. But what does it lose? It was formed by merely roasting lead in the air, and the something which it loses must therefore have been derived from the air. If the red lead is heated in a tube a gas is given off which is collected and tested—how? with a taper or glowing splinter as it is to be supposed that the gas will support combustion if, as is to be expected, it is the active constituent of air. The *discovery* of the active constituent of air is thus made! If air consist of this gas and that which remains after exposing phosphorus or iron in air, then by adding to such residual air as much of the gas from red lead as was withdrawn, air should be re-obtained; this is found to be the case. The names of the two gases are now *for the first time* stated, and an easy method of preparing oxygen is demonstrated, such as that of heating chlorate, but without any explanation. The conclusion previously arrived at, that probably in all the cases previously studied of changes occurring in air, the oxygen is the active substance, may now be verified by burning or heating in oxygen the substances which had been burnt in air.

So much having been learnt of the chemistry of air, the study of the pressure exercised by air may next be taken up, and the common pump, the force pump, the barometer and air currents may be discussed and explained. Now-a-days the charts given in the daily papers, and the Ben Nevis and Glycerin barometer readings quoted in the *Times* make it particularly easy to explain the barometer. The pupils should be led to make barometer curves.

PROBLEM IV. *To Determine the Composition of Chalk.*—The discovery of the *composition* of the air in the course of experiments made with the object of determining the nature of certain changes naturally suggests that the attempt be made to ascertain the composition of other things by studying the changes which they undergo. Chalk is known to give lime when burnt, and experiments made in Stage III. have indicated that chalk loses something when burnt—the idea that an invisible something is given off is especially probable after the experiments with red lead have been made; so it is decided to heat chalk strongly, but before doing this chalk and lime are examined comparatively. Chalk is not observed to be altered by water; on shaking it up with distilled water and evaporating some of the filtered liquid in a weighed dish, very little residue is obtained—so it is established that it is but very slightly soluble in water. Lime is slaked, weighed quantities of lime and water being used; the retention of a considerable amount of water, even after exposing the slaked lime in the drying oven, shows that the slaking involves a definite change in composition—that slaked lime is lime and water. The solubility of the lime is next determined, and found to be considerably greater than that of the chalk. It is found that chalk is but very slightly altered in weight when heated over a gas flame, and that it is only when it is strongly heated that it is converted into lime: so the chalk is strongly heated in an iron tube in a Fletcher blowpipe furnace, when gas is freely given off. This is tested with a taper, which it extinguishes, so it cannot be oxygen, but may be nitrogen; if it be nitrogen, when mixed with oxygen in the proportion of 1 to 4, it should give air, but this is found not to be the case; so evidently it is a peculiar gas, and may be called chalk gas. If chalk consist of this gas and lime it should be possible to reproduce chalk from them; so the gas is passed through a small weighed tube containing lime and the tube is found to get heavier. But lime and chalk are so much alike that it is difficult to say that chalk is formed; perhaps dissolved lime will act similarly; the gas is therefore passed into or shaken up with lime water. The precipitate which forms looks like chalk, and probably is, but this remains to be decided. The discovery of this behaviour of chalk gas, however, is important as affording a means of again comparing the gas from chalk with nitrogen. In working with lime water it is scarcely possible to avoid noticing that a film forms on its surface; by exposing a quantity of the lime water a considerable amount of the precipitate is obtained; its resemblance to chalk is noted, and the possible presence of chalk gas in air is thus suggested; but in view of the absence of proof of the identity of the precipitates with chalk a decision is reserved. The discovery is made, however, that air contains something besides oxygen and nitrogen.

It being thus established that chalk consists of two things, lime and chalk gas, at this stage it is pointed out how firmly these two constituents hold to each other in the chalk. The absorption of the gas by the lime—its entire disappearance in fact—is commented on. Accurate determinations of the loss of weight on heating crystallised chalk (calc spar) should at this stage be carried out before the class, if not by the pupils, so that the numbers may be quoted and that it may become impressed on them that the proportions in which the lime and chalk gas are present is constant. Their attention may be recalled to the oxides previously studied, it being pointed out that on inspection these afford no indication that they contain oxygen: that here again the gas entirely loses its individuality on entering into union or combining. That oxides contain their constituents in fixed proportions may be demonstrated experimentally by oxidising finely-divided copper and determining the increase in weight, lime being used as drying agent. In this way the characteristics of *compounds* are elucidated. Then the comparison may be made with air and the fact made clear that it behaves as a mere mixture. Still no reference should be made to elements.

PROBLEM V. *To Determine what Happens when Organic Substances are Burnt.*—The experiments thus far made have shown that phosphorus and a number of metals burn in the air because they combine with the oxygen, forming oxides, heat being given out *as a consequence;* but that chalk when burnt is split up or decomposed into lime and chalk gas, this result being a consequence of the heating alone, the air having nothing to do with it. It remains to ascertain what happens when organic substances are burnt, as these give no visible product beyond a little ashes. As in all cases when vegetable or animal substances are burnt a certain amount of "char" is obtained, which then gradually burns away, charcoal or coke is first studied. It having been discovered that the oxygen in air is the active cause of burning in many cases, it appears probable that the air is concerned in the burning of

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe, Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

charcoal, coal, &c. As when once set fire to these continue to burn, the charcoal is at once heated in oxygen: it burns, but no visible product is formed: it therefore follows that if the charcoal is oxidised the oxide must be an invisible gas. How is this to be tested for? What gases are already known to the pupil? How are these distinguished? Oxygen is excluded. Is it perhaps nitrogen, and is not perhaps the nitrogen in air merely used-up oxygen as it were, produced by the burning of organic substances? Or is it perhaps that gas which was found in the air along with oxygen and nitrogen, and which turned lime water turbid? This last being an easy test to apply is at once tried; the lime water is rendered turbid, and so to leave no doubt a sufficient amount of the gas is prepared and passed into lime water, the precipitate is collected, and the loss it suffers on heating is determined and found to agree with that suffered by the precipitate prepared from chalk gas. Finally, to ascertain whether the product is really heavier than the charcoal burnt, as in the case of the metals previously studied, the charcoal is burnt in oxygen in a tube connected to a flask containing milk of lime with a lime-drying tube attached to it; the tube is weighed before and after burning. Thus the discovery is made that chalk gas is an oxide of carbon, and that chalk consists of at least three things.

It may be objected that to make the experiment in this manner takes too much time; but to this it may be answered that such experiments are precisely of the kind of those made in actual practice, and that they exercise a most important influence in teaching the pupils to take nothing for granted, never to jump at conclusions, and to rest satisfied if they progress surely, however slow the advance may be.

A number of organic substances may now be burnt, and the gas passed into lime water; chalk gas is found in every case to be a product, and hence the presence of a common constituent—carbon in all is established. In making these experiments the formation of a liquid product is observed, so it is evident that chalk gas is not the only product, or carbon their only constituent.

Food materials generally having been found to contain "carbon," as they are obviously in some way destroyed within the body, and it is known that air is necessary for life, the question arises, what becomes of food, and why is air necessary for life? Is the food, perhaps, in large part "burnt up" within the body, thus accounting for the fact that our bodies are always warm? The characteristic product of combustion of carbonaceous substances is therefore tested for by breathing into lime-water. The discovery thus made affords an opportunity for a digression and for explaining how plants derive their carbon from the air.

Problem VI. *To Determine what Happens when Sulphur is Burnt.*—From the results of the experiments with carbon, it appears probable that the disappearance of sulphur when burnt is also really due to its conversion into a gaseous oxide, so it is kindled and introduced into oxygen: if it be burnt over water in a bell jar in a spoon passing through the stopper (a rubber cork), the water is seen to rise; if, on the other hand, it be burnt in a dry flask closed by a rubber cork carrying a guage-tube, as suggested by Hofmann,* the volume is seen to be almost unchanged after combustion. It follows, therefore, that the sulphur and oxygen unite and form a soluble product. Sulphur is next burnt in a tube in a current of oxygen, and the gas is passed into water; a solution is thus obtained having the odour of the gas and sour (acid) to the taste. The fact that carbon and sulphur—both non-metals—behave alike in yielding gaseous oxides suggests that a comparison be made of their oxides: so the acid solution is added to lime water; a precipitate is formed which re-dissolves on adding more of the sulphur gas solution; on the other hand, on adding the lime water to the acid liquid, this latter after a time loses its characteristic smell. There can be no doubt, therefore, that the sulphur gas does in some way act upon the lime. The experiment is then made of burning the sulphur in a weighed tube containing lime; the weight increases, so that no doubt remains that sulphur, like carbon, forms an oxide when burnt. The discovery that the addition of more of the sulphur oxide leads to the dissolution of the precipitate which it first forms in lime water, suggests trying the effect of excess of the carbon oxide on the lime water precipitate; this is done, and the discovery is made that the precipitate gradually dissolves. The solubility of the new substance may then be determined by passing the gas into water containing chalk in suspension, filtering, and evaporating. This leads to the observation that a precipitate is formed on heating the liquid, and this is soon found to be chalk. An opportunity is thus afforded of explaining the presence of so much "chalk" in water; of demonstrating its removal by boiling and by lime water; and the effect it has on soap.

The observation that the oxides of both carbon and sulphur combine with lime suggests trying whether the one will turn out the other, so the solution of the sulphur oxide is poured on to chalk; effervescence is observed, and on passing the gas into lime water a precipitate is obtained. The production of this effect by the *acid* solution suggests trying common vinegar—a well-known *acid* substance. This also is found to liberate chalk gas, and the discovery of an easy method of preparing chalk gas is thus made. The oxide formed on burning phosphorus, having previously been found to give an acid solution, is tried, and it is found that it also liberates chalk gas. As a good deal of vinegar is found to give very little chalk gas, the question arises, Are there not acids to be bought which will have the same effect and are stronger and cheaper; On inquiry it is found that sulphuric acid or oil of vitriol, muriatic acid or spirits of salts, and nitric acid or aquafortis may be bought, and that these all act on chalk. The behaviour of chalk with acids affords a means of testing the lime water precipitate obtained in working out Problems IV. and V. In this manner the pupil is led to realise that certain agents may very readily produce effects which are only with difficulty produced by heating — that the *chemical agent* may produce very powerful effects. The ready expulsion of the carbon oxide of the chalk suggests that other substances not yet studied, such as the metals, when treated with acids may behave in a special manner which will afford information as to their nature. At this point, prior to making the experiments with the acids, an explanation may be given of the names *oil of vitriol*, *spirits of salts*, and *aquafortis*; the processes by which they are made may be described and illustrated, without, however, any attempt being made to explain them from the chemical point of view. The sulphuric acid should be made from green vitriol, and its behaviour on dilution should be demonstrated as well as its use as a drying agent.

Problem VII. *To Determine what Happens when Metals are Heated with Acids.*—Iron, zinc, lead, tin, copper, and silver may be taken. On pouring diluted oil of vitriol on to iron or zinc, the metal dissolves with effervescence; the gas is collected, and, when tested, is found to burn. Thus, a new gas is discovered, differing from all which have previously been studied, inasmuch as it is combustible; in order not to interrupt the study of the action of acids on metals, however, its further examination is postponed for a while. Resuming the experiments with metals, lead, tin, copper, and silver are found not to be acted upon by diluted oil of vitriol.

Muriatic acid, in like manner, dissolves iron and zinc and also tin with effervescence, and the gas which is given off in each case exhibits the same behaviour as that

* By burning carbon also in this way a most effective demonstration is given of the fact that no loss or gain of matter attends the change, and that only heat escapes; the results in the case of carbon and sulphur are particularly striking, as the products are gaseous and invisible.

obtained from iron or zinc and diluted oil of vitriol. Lead, copper, and silver are not appreciably affected.

Aquafortis is found to dissolve not only iron and zinc but also copper, lead, and silver, and to convert tin into a white substance—to attack all the metals in fact, thus justifying its name. The gas which is given off as the metal dissolves is observed to be coloured; when it is collected over water, however, it is seen to be colourless, and to become coloured on coming into contact with air—oxygen and nitrogen are, therefore, added to portions of the gas over water. In this manner not only is a new gas discovered, but also a test for oxygen; and opportunity is afforded of here calling attention to the fact that air behaves exactly as oxygen, that the oxygen in air appears to be unaffected by its association with nitrogen—that, in fact, it is uncombined. From these experiments it is obvious that metals and acids interact in a variety of ways. Finally, the dissolution of gold and platinum by aqua regia may be demonstrated.

Problem VIII. *To Determine what Happens when Oxides are Treated with Acids.*—In the course of the previous experiments a number of oxides have been prepared by burning various metals in air; these are found to be unchanged by water. The discovery that acids act on metals suggests a trial of the effect which acids will have on their oxides; so the oxides of zinc, iron, copper, and lead are submitted to the action of the three acids previously used. Sulphuric acid is found to dissolve zinc oxide, iron rust, and copper oxide, but no gas is evolved; excess of the oxide may be used, and the filtered liquid concentrated; the crystals which separate may be examined and compared with those obtained by dissolving the metal in sulphuric acid, &c. Litharge apparently is not changed by sulphuric acid, but red lead is, although not dissolved. Muriatic acid being used, all the oxides are found to dissolve, and in the case of red lead a greenish yellow gas is given off, possessing a most disagreeable smell; this is noted as a case for study. The product from the lead oxides is observed to crystallise out from the hot liquid on standing, so the undissolved original product is boiled up with water and the solution is filtered, &c. Attention is thus directed to the difference in solubility of the products. Next, aquafortis is used; again, all are dissolved, except the red lead, which, however, is obviously altered. In the case of the lead oxides the product is again less soluble than those afforded by the other oxides, but more soluble than the product obtained on using muriatic acid. The pupil has already been led to realise that of two substances capable of acting on a third, such as chalk gas and sulphur gas, which both combine with lime, one may be the stronger, and may turn out the other, sulphur gas turning out chalk gas from chalk. A comparison of the three acids with the object of ascertaining which is the strongest is therefore suggested—the metal or oxide is dissolved in one of the acids, and the others are then added. No positive result is obtained in the case of zinc, iron, or copper, but the solution of lead in nitric acid is precipitated by muriatic and by sulphuric acid; the former precipitate is found to dissolve in boiling water and to crystallise out in exactly the same way as the substance obtained from lead oxide and muriatic acid. The sulphuric acid product is found to be almost insoluble in water, and also in muriatic and nitric acids; these observations make it possible, by examining the behaviour towards muriatic and nitric acids of the products of the action of sulphuric acid on the lead oxides, to establish the fact that the product is the same whether lead be dissolved in nitric acid and sulphuric acid be then added, or whether either of the oxides be treated with sulphuric acid. It is further evident that those acids which give difficultly soluble or insoluble products act with difficulty, if at all, on the metal. Other metals besides those mentioned may be now studied, and, a solvent being found, the acids which do not dissolve the metal may be added to the solution. In this way, for example, the chloride test for silver is discovered.

In experimenting with acids the pupils can hardly fail to stain their clothes and their fingers. The observation that acids alter colours serves to suggest experiments on the action of acids on colours, especially those of leaves and flowers. The use of litmus, methyl orange, cochineal, &c., may then be explained. As various oxides have been found to "neutralise" acids, the study of their effect on the colours altered by acids is suggested. Lastly, a few experiments with vegetable and animal substances, sugar, &c., may be made, which demonstrate the corrosive action of oil of vitriol and aquafortis.

Problem IX. *To Determine what Happens when the Gas obtained by Dissolving Iron or Zinc in Sulphuric or Muriatic Acid is Burnt.*—The gas has been observed to burn with a smokeless odourless flame. To ascertain whether, as in all other cases of combustion previously studied, the oxygen of the air is concerned in the combustion, a burning jet of the gas is plunged into a dry cylinder full of oxygen, in which it is not only seen to continue burning, but it is also noticed that drops of liquid condense on the cylinder above the flame; this immediately suggests that the product is a liquid. The jet is found to be extinguished in nitrogen, so evidently when the gas burns it forms an oxide. The experiment is repeated and the gas burnt in a bell jar full of oxygen over water; the water rises as the combustion proceeds, proving that the oxygen is used up. To collect a sufficient quantity of the product for examination the dried* gas is burnt at a jet underneath a Florence flask through which a stream of cold water is allowed to circulate: the neck of the flask is passed through the neck of a bell jar and the flask and bell jar are clamped up in an inclined position, so that the liquid which condenses may drop into a small beaker placed below the rim of the jar. What is the liquid? It looks very like water, and is without taste or smell. Is it water? How is this to be ascertained? What are the properties of water? The knowledge previously gained here becomes of importance. It has been observed that frozen water melts at 0° Centigrade, that water boils at 100°, and that 1 c.c. weighs 1 grm. at 4° C.; so the liquid is frozen by the ice-maker's mixture of ice and salt, a thermometer being plunged into it so that the solid ice forms on the bulb; the melting-point is then observed. Subsequently the boiling-point is determined, a little cotton-wool being wrapped around the bulb of the thermometer. Lastly, the density of the liquid may be determined. It is thus established that the gas yields water when burnt, and the name of the gas may now, *for the first time*, be mentioned and explained. The results thus obtained leave little doubt that water is an oxide of hydrogen; but in order to place this beyond doubt it is necessary to exclude nitrogen altogether. How is this to be done? Red lead is known to consist of lead and oxygen only, and readily parts with a portion, at least, of its oxygen; so dried oxygen is passed over red lead, which is then gently heated. Again a liquid is obtained which behaves as water, so there can be no doubt that water is an oxide of hydrogen. Water is not obtained on merely mixing oxygen and hydrogen; it is only produced when combustion takes place. To start the combustion a flame is applied to a small quantity of a mixture of the two gases: a violent explosion takes place. An opportunity is here again afforded of calling attention to the entire change in properties which takes place when the compound is formed. On heating red lead in hydrogen, lead is obtained, although on heating it alone it loses only a portion of its oxygen, and the "reduction" takes place very readily; evidently, therefore, hydrogen is a powerful agent. This observation suggests further experiments. Will it not be possible to remove oxygen by means of hydrogen from other oxides which are not altered on heating? and will not

* The importance of drying the gas is realised without difficulty, as previous observations have shown that the air is moist, and, as the gas is given off in presence of water, lime may be used.

other combustible substances besides hydrogen remove oxygen from oxides?

Problem X. *To Determine what Happens when Hydrogen and other Combustible Substances are Heated with Oxides.*—Zinc oxide, iron rust, and copper oxide are now heated in a current of hydrogen: the first remains unaltered, the other two are seen to change, a liquid being formed which it cannot be doubted is water; the copper oxide evidently becomes reduced to copper. Is the iron rust similarly reduced to the metallic state? How is iron to be tested for? Iron is attracted by the magnet, and dissolves in diluted oil of vitriol with evolution of hydrogen. Applying these tests, no doubt remains that the iron rust is deprived of its oxygen.

Litharge and copper oxide may then be mixed with soot or finely-powdered charcoal and heated in tubes; gas is given off which renders lime-water turbid, and metallic lead or copper is obviously obtained. It is thus established that some, but not all, oxides may be deprived of their oxygen by means either of hydrogen or carbon. Opportunity is here afforded of explaining the manufacture of iron.

Several dried combustible organic substances, sugar, bread, and meat, may now be burnt with copper oxide in a tube, the fore part of which is clean and is kept cool: liquid is seen to condense, while "chalk-gas" is given off; the liquid has the appearance of water, and sufficient may easily be obtained to ascertain whether it is water. The presence of hydrogen in organic substances is thus discovered; its origin from water may now be explained, and the double function of water in the plant and animal economy may be referred to—viz., that it both enters into the composition of the animal and plant structure, and also acts as a solvent. The combustion of ordinary coal-gas, of alcohol, of petroleum, of oil, and of candles, may then be studied, and the presence of hydrogen in all of these noted.

(To be continued).

CORRESPONDENCE.

THE AMINES SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—Having recently attended a demonstration of the above process at the Wimbledon works, on the occasion of a meeting of the members of the Society of Municipal Engineers, I read your communication (Chemical News, vol. lx., p. 157) with interest.

We are accustomed to see extravagant accounts of the marvellous effects of "chemicals" in the columns of Dailies; but the minds of chemists are not so easily disturbed, and it is in your columns, "par excellence," that the real grit of an invention should be ground out. With that object in view I venture to make some comments upon this process.

You say the process you witnessed was as follows:—

"Milk of lime was mixed in the proportion of about $4\frac{1}{2}$ lbs. per 1000 gallons, along with about 18 ozs. of trimethylamine. It does not sufficiently appear whether these 18 ozs. are to be actual trimethylamine or brine, &c., in which such a quantity of trimethylamine has been found to be present."

Herr Wolheim stated at Wimbledon that herring-brine contained two-thirds of a percentage of trimethylamine. That being so, to obtain 18 ozs. of trimethylamine we should need 2727 ozs. of the brine. If the 18 ozs. are to be read as meaning brine, these 18 ozs. of a two-third's per cent solution would contain 0·118, or just over $\frac{1}{10}$ oz. of trimethylamine for each 1000 gallons of sewage, or 0·051 grains per gallon. Say we have a flow of three millions of gallons of sewage, and that the 18 ozs. are trimethylamine, then about 50,000 gallons of brine would be used up daily.

Here we have the horns of a dilemma, and I should like to know upon which horn Herr H. Wolheim prefers to rest.

That Dr. Klein found an effluent after treatment with between 70 and 80 grains per gallon of lime to be sterile does not appear to me to be remarkable, and, of course, if it be sterile from its alkalinity it would not decompose upon keeping.

I should almost as much expect to find living organisms in, say, sulphuric acid as in such an alkaline liquid.

In such an effluent there would be much putrescible matter in solution, and if the fluid were diluted with ten times the bulk of ordinary river water, with its usual microbian populations, fermentative changes would most likely be set up. It is like passing through a second period of juvenility to be fighting the old lime fallacy; a ghost long since laid has again raised its head, but this time *Cum grano salis*.—I am, &c.,

Cyclops.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 10, September 9, 1889.

The Fixation of Atmospheric Nitrogen.—M. Berthelot.—The author holds that the opinion that the free nitrogen of the atmosphere plays no part in vegetation or in agriculture has been abandoned, except, possibly, by M. Schlœsing, who does not express himself decidedly upon this point. This change of views M. Berthelot ascribes to the researches which he has carried on for the last six years, and which have led to other investigations, such as those of G. Ville, of MM. Hellriegel and Willfarth, of M. Dehérain, and M. Joulie, &c. The active agents in the fixation of nitrogen he considers to be certain microbia. The causes why, in some experiments, the results obtained have been negative may be the exposure of the soil to the deleterious vapour of mercury, or the application of a heat sufficient to kill the microbia, or operating on soils already saturated with nitrogen.

Observations on the Formation of Ammonia and of Volatile Nitrogenous Compounds at the Expense of the Vegetable Mould and of Plants.—M. Berthelot.—Vegetation is constantly attended by an exhalation of ammonia and of other volatile compounds. This exhalation, though very trifling, deserves attention, because the volatile nitrogenous compounds emitted by living beings are often possessed of an extremely active poisonous property, even as regards the very living beings by which these compounds have been secreted.

The Nitrification of Ammonia.—Th. Schlœsing.—The nitrification of the ammonia applied to a hectare of land may be very rapidly accomplished when it is favoured by the nature of the soil, its humidity, and its temperature. In a future communication the author proposes to examine the case when the ammonia is applied in the free state or as carbonate in too large a quantity, when it becomes injurious to the nitric ferment.

The Spectrophotography of the Invisible Parts of the Solar Spectrum.—Ch. V. Zenger.—A single prism of rock-salt, combined with two prisms of anethole increase the dispersion ninefold, and the red part of the

spectrum is six times more dispersed between A and D than by a prism of rock-salt.

Researches on the Sulphites.—P. J. Hartog.—The author describes the sodium-ammonium sulphite-bisulphite, a compound obtained by passing a current of gaseous ammonia into a saturated solution of sodium bisulphite. He also describes an isomeric modification of sodium metasulphite.

A New Monobromated Camphor. On the Constitution of the Monosubstituted Derivatives of Camphor.—P. Cazeneuve.—The mono-bromo- substitution compound presents similar properties to the chloro-derivative obtained by means of hypochlorous acid. The bromine has been substituted for hydrogen in a CH_2 of the nucleus.

On Phenol-disulphonic Acid.—J. Allain Le Canu.—The author has obtained this compound by placing sulphuric acid of sp. gr. 1·84 and pure phenol over each other in a bell exhausted of air.

Influence of Gypsum and Clay on the Preservation of Nitrogen, the Fixation of Atmospheric Nitrogen, and Nitrification.—M. Péchard.—The addition of baked gypsum to sandy soils containing nitrogen greatly reduces the loss of nitrogen. Clay was found to have a similar effect.

Manufacture of Red Glass for Windows.—Ch. Guignet and L. Magne.—The authors have studied the composition of old coloured glasses of the twelfth and thirteenth centuries. They give diagrams showing the structure of some specimens.

No. 13, September 23, 1889.

This number contains no chemical matter.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xx., No. 1.

New Apparatus for the Concentration of Extracts in a Vacuum.—L. A. Adrian.—This paper cannot be reproduced without the two accompanying plates.

On the Sulphur Compounds of the Cruciferæ.—W. J. Smith (*Annales Agronom.*).—To determine the myronic acid the quantity of sulphuric acid pre-existing in the seeds before the myronate is split up must be determined. To this end the action of the ferments contained in the seeds must be arrested by treating them with hydrochloric acid at 0·3 per cent. The author has operated on the seeds of black mustard, determining the sulphur present in the state of sulphuric acid, and then the total sulphur. Rather more than one-third of the total sulphur belongs to the albumenoids and the rest to the myronic acid.

House Filters and Potable Waters.—A. J. Snijers (*Deutsch. Med. Wochenschrift*).—The author states that fine sea-sand, washed and raised to a high temperature, arrests almost all the organic germs and bacteria. He compares in this respect (removal of living organism) the value of the filters of Pasteur, Chamberland, and of Maignen. The former retains its sterilising power for at least two months, but its action upon the chemical impurities is slight. Without pressure the filtration is too slow, scarcely a litre an hour. The Maignen filter has less action on bacteria, and loses its sterilising power in a few days. It yields 40 litres in twenty-four hours. The filtrate contains one-half less solids than the original water, the organic matter disappearing almost entirely. The action is perfect for salts of lead and iron, good for nitrates and ammonia, null for chlorides.

Separation of Strychnine and Brucine.—J. E. Gerock (*Archive der Pharm.*).—The alkaloids are precipitated in heat from their neutral solution by picric acid. The mixture is let cool, and, after being let stand for a sufficient time, the picrates are thrown upon a tared filter, washed in cold water until the liquid runs through colourless, dried at 105°, and weighed. As much as possible of the precipitate is removed from the paper and put in a beaker. On the other hand, the filter is repeatedly washed with nitric acid of sp. gr. 1·056 previously heated in the water-bath. The brucine picrate which remained adhering to the paper is thus destroyed. The nitric acid is then poured upon the precipitate previously removed, and it is heated on the water-bath for some time. It is then exactly neutralised, a trace of acetic acid is added (strychnine picrate, though soluble in nitric acid and in the alkalies, is insoluble in dilute acetic acid), and it is let cool. Lastly, the strychnine picrate is thrown on the filter already used, washed, dried, and weighed. The difference of the two weights shows the quantity of brucine present in the mixture.

A New Salt bordering on Potassium Ferrocyanide.—F. Mahla (*Berichte*).—If we exhaust with cold water the mixture which has served for purifying coal-gas and submit the liquid to fractionated precipitation with ferric chloride, the last portions, instead of prussian blue, yield a deep violet precipitate. This precipitate, if treated with alkalies, yields ferric oxide, and a yellow solution which, after neutralisation, gives, with ferric chloride, a violet precipitate, with copper salts a parrot green, and with salts of cobalt a fresh red.

Archives Neerlandaises des Sciences Exactes et Naturelles.
Vol. xxiii., Parts 3 and 4.

Experimental and Theoretic Study on the Conditions of Equilibrium among the Solid and Liquid Combinations of Water with Salts, especially with Calcium Chloride.—H. W. Bakhuis Roozeboom.—This memoir, which extends to 150 pages, discusses in succession the various hydrates of calcium chloride and their solubilities, the general solubility of salts, the phenomenon of supersaturation, and the condition of salts in a saturated solution; the tension of the different systems composed of calcium chloride and water; the conditions of equilibrium of these systems; the thermo-dynamic relations for the vapour-tensions of the different systems of water and of a salt; application to the case of calcium chloride and a general review of other salts; and lastly, thermo-dynamic relations for the concentration of solutions in equilibrium with a solid salt and vapour of water.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Separation of Sulphides.—We are directed in most works on qualitative analysis in the H_2S group, for the separation of the sulphides of As, Sb, and Sn from Hg, Cu, Pb, Bi, and Cd, to digest the precipitate in $(H_4N)_2S$ (yellow), in which As, Sb, and Sn are soluble, while the others are not so (or only slightly, as Cu). As, after repeated trials, I have never yet had good success in this stage of the analysis, I would be obliged to any chemist who has worked it satisfactorily for the *minor details* of the process, including directions for making the $(H_4N)_2S$ as used by him in it.—P. D.

Molecular Volumes.—Can any of your readers give me any information as to the recent experiments mentioned in the following question, taken from a chemistry examination paper? "The molecular formulæ of the elements are generally taken as representing two volumes of gas: thus H_2 is said to represent two volumes of hydrogen, while the elementary symbol H is taken as the unit associated with the idea of one volume. Show from recent experiments that this is inadmissible, and that the gaseous atom cannot be supposed to occupy one volume."—STUMPED.

TO CORRESPONDENTS.

Ibn. Menenek.—Reference to the indices of our back volumes will give the desired information.

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PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that The Actien Gesellschaft für Anilin Fabrikation, of Berlin, in the Empire of Germany, has applied for leave to amend the Specification of Letters Patent No. 4415 of 1884, granted to Gerard Wenzeslaus von Nawrocki for "Improvements in the manufacture of colouring matters."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 2nd October, 1889.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed),
H. READER LACK,
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THE CHEMICAL NEWS.

Vol. LX. No. 1560.

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A WATER-JACKETTED FLEXIBLE TUBE.

By FREDERICK J. SMITH.

It is often convenient to conduct gases through flexible tubes, but the convenience is not without its disadvantage, since some gases diffuse readily through rubber. Having to deal with electrolytic gas in a research on explosions in tubes, and believing that some error would be introduced by the use of rubber tubes as usually employed, I devised a flexible tube almost quite free from the disadvantage mentioned. As the device may possibly be of use in the laboratory, I venture to send a description of it to the Chemical News.

A length of small rubber tube is drawn through another tube of equal length but of greater diameter; each end is furnished with a small length of glass tube fitting the smaller tube; one end is bound off with cord, then the space between the inner and outer tube is filled with water or any liquid required; the other end is then bound off. By this means a water-jacketted flexible tube is easily constructed.

Millard Laboratory, Trinity College,
Oxford, October 8, 1889.

ON THE REACTION OF BENZOQUINONE WITH POTASSIUM CYANIDE.*

By S. A. SWORN, B.A., Assoc. R.C.Sc.L.

Hydrocyanic acid does not form a compound with benzoquinone. The latter body, however, readily combines with potassium cyanide to form a dark green body, which is obtainable only in aqueous solution. One molecule of the quinone combines with one of the cyanide. Anthraquinone does not form such a compound. Hydrocyanic acid (but no quinone) is given off when the solution is boiled, and quinone is liberated by the addition of silver nitrate solution.

CONTRIBUTIONS TO THE STUDY OF PURE FERMENTATIONS.*

By Professor PERCY F. FRANKLAND, Ph.D., B.Sc.
GRACE C. FRANKLAND, and J. J. FOX.

The authors point out how very few of the bacterial fermentations hitherto studied have been performed with ferments of undoubted purity, as well as the insufficiency of the description of the morphological characters of the organisms in question. Such scanty descriptions generally render it impossible for other investigators to know whether they are dealing with the same or with different ferments.

The authors have isolated and fully characterised by the modern methods of cultivation an organism, a small bacillus, which sets up fermentation not only in solutions of glucose cane-sugar, milk-sugar, and starch, but also in solutions of mannite, glycerin, and calcium glycerate. The fermentations of mannite and glycerin have alone been so far studied.

* Read before the British Association, Section B Newcastle Meeting.

In each case the products are essentially the same, viz., principally ethyl, alcohol, and acetic acid, together with smaller quantities of formic acid and a trace of succinic acid. The alcohol was separated by distillation and the quantity determined, whilst the several acids were estimated by conversion into their barium salts in the case of the acetic and formic acids, whilst the succinic acid was extracted and weighed in the free state.

In the case of the mannite fermentations it was found that the amount of alcohol and acetic acid formed stood in the proportion of two molecules of alcohol to one molecule of acetic acid, whilst in the glycerin fermentations there were three molecules of alcohol to one of acetic acid.

Of particular interest is the fact that the organism has no fermentative action on dulcite, the isomer of mannite, which thus furnishes a very striking instance of the selective power of micro-organisms between the most closely allied isomeric bodies. The authors were also unable to cause the organism to ferment solutions of either erythrite, ethylene glycol, calcium, lactate, tartrate, citrate, or glycollate.

In view of the characteristic products—ethyl, alcohol, and acetic acid—of the fermentations, the authors propose for the organism the name of *Bacillus ethaceticus*.

MAGNESIUM AS A REAGENT.

By H. N. WARREN, Research Analyst,

Magnesium, both on account of its purity, and, at the same time, the speed with which it facilitates reduction, either in the moist or dry way, causes it to rank high, if not the first, among reducing agents. Thus, for instance, on account of its purity from arsenic, no agent is, perhaps, better suited for the elimination of pure hydrogen when using Marsh's test for that substance. Secondly, its absence from iron renders it one of the safest reagents for the reduction of ferric salts previous to titration. The speed of reduction, at the same time, being about three times that of zinc, and giving practically no reaction with potassic ferricyanide, the desired absence of both phosphorus and sulphur may also be relied upon. The ease with which it precipitates, from solutions, for instance, zinc, distinguishes it practically from all other metals, separating the same so perfectly that, if to a solution of zinc acetate containing also metals of the fourth group some pieces of magnesium be introduced, and the solution brought to a state of ebullition, the whole of the zinc is thus separated, so as to cause, after the introduction of the necessary reagents to retain in solution the magnesium salts, no precipitate on the addition of ammonium sulphide.

Several samples of zinc ashes containing, as impurities, calcium, magnesium, and other carbonates were quickly assayed by this method, and the zinc estimated in the metallic form.

Its general behaviour with iron salts is somewhat more complex, but, strange to say, from a solution containing a chromic salt, the iron may, with a slight experience, be entirely separated. Take, for example, a sample of chromeisen, to the acid solution of which has been added a sufficiency of sodium carbonate to replace the combined acid. To the precipitated carbonate is added acetic acid in slight excess; if, now, to the acetic acid solution thus formed about 1 grm. of magnesium is introduced, a somewhat violent reaction takes place, the ferric salt becoming almost instantly reduced, and the reaction thus terminating. On the application of heat to the solution the liquid now changes from the deep green characteristic of chromium chloride to a slight pink, thence to a red, violet, and gradually to a pure green, thus assuming its original tint, during which time the iron contained in solution has been precipitated upon the magnesium in a

somewhat coherent form, not unfrequently contaminated with oxide of the same. This is to be withdrawn from the solution containing the chromium, boiled with a few drops of HNO_3, and tested for the presence of iron by means of potassium sulphocyanide. As a reagent in the dry way magnesium reduces all metals with the exception of the alkalies and alkaline earths, and may possibly aid in the decomposition of the latter, provided a suitable combination of the same could be obtained.

As an exception to reduction in this line may be mentioned the powerful manner in which it attacts molybdic anhydride, when fused with the same, the combination being so intense as to be accompanied with loud detonations.

Even the refractory substances, silica and boric anhydride, may be also reduced when intensely heated in closed vessels with the same.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

ANALYTICAL STUDIES ON PHOSPHODODEKAMOLYBDIC ACID, THE CONDITIONS OF ITS FORMATION, AND ITS SEPARATION AS AN AMMONIUM SALT.

By Dr. FRANZ HUNDESHAGEN.

(Continued from p. 178).

Save for trifling irregularities due to errors of observation, the numbers found agree with the values given above; they are in general rather larger. The precipitates have all essentially an equal and a normal weight. The formation of ammonium phosphomolybdate is completely prevented by $1900-26=1874$ mols. of free NO_3H, but the dissociated compound is separated by an equivalent quantity of nitric acid in excess.

In a solution of a phosphate which contains an excess of nitric acid there must exist, besides the quantity of MoO_3 required for forming phosphododekamolybdic acid, a mol. MoO_3 to every $\frac{1874}{12}=156$ mols. of free nitric acid in excess, in order that the separation of the phosphoric acid may be complete.

5. *Influence of the Proportion of Foreign Salts in the Solution upon the Formation and Separation of the Ammonium Phosphomolybdate.*

As an excess of phosphate or molybdate in a neutral saline mixture involves an increased consumption of acid in the precipitation of the ammonium phosphomolybdate, the presence of other salts of the polybasic acids has a similar action, whilst indifferent salts of monobasic acids, such as the chlorides and bromides, have no perceptible influence upon the course of the reaction. The author therefore confines himself to studying the phenomena in the case of ammonium sulphate and of borax.

On precipitating a neutral solution of ammonium nitrate containing the components of phosphododekamolybdic acid with standard sulphuric acid there were required likewise 23 mols. for the separation of the ammonium phosphomolybdate just as is the case with monobasic nitric acid, though sulphuric acid is bibasic; the conclusion of the reaction was not distinct.

The formation of ammonium phosphomolybdate was attended with the formation of 23 mols. of ammonium hydrosulphate. If the solution already contained sulphate (the proportion of phosphate and molybdate being equal) the consumption of sulphuric acid was still greater, and the greater the richer the solution in sulphate.

Though the distinct determination of the point at which the formation of phosphomolybdate was completed was very difficult on account of the extreme retardation of the separation from solutions containing sulphate, even if nitric acid was added, the following regularities were perceptible:—

The precipitation of the ammonium phosphomolybdate could not be regarded as completed until the typical 23 mols. of hydrosulphate were formed, and when about the tenth part of the extraneous sulphate had been converted into hydrosulphate. It was a matter of indifference whether nitric or sulphuric acid was used for precipitation, and whether ammonium nitrate was present or not.

For precipitating the ammonium phosphomolybdate from 0·010 grm. phosphoric acid and 0·243 grm. molybdic acid from a neutral solution containing—

1	5 grms.	$SO_4(NH_4)_2$	$=269$ mols.
2	5 ,,	,,	$=269$,,
3	10 ,,	,,	$=538$,,
4	10 ,,	,,	$=538$,,

there were required—

1	0·65 grm.	NO_3H	$=73$ mols.
2	0·48 ,,	SO_4H_2	$=35$,,
3	0·88 ,,	NO_3H	$=99$,,
4	0·68 ,,	SO_4H_2	$=50$,,

Nos. 3 and 4 contained also NO_3NH_4.

These latter quantities of acid would have produced along with one mol. of $12MoO_3.PO_4(NH_4)_3$ and 12 mols. H_2O:—

	NO_3NH_4.	$SO_4H(NH_4)=n$.	$SO_4(NH_4)_2=m$.	$n-23:m$
1	73	50	219 mols.	1 : 8
2	—	47	257 ,,	1 : 10·7
3	99	76	462 ,,	1 : 8·7
4	—	77	511 ,,	1 : 95
			In mean	1 : 9·2

The number of the mols. of hydrosulphate formed ($=n$), minus 23, is to the unchanged neutral sulphate (m) in the mean as 1 : 9·2. Therefore, as already said in this reaction, 23 mols. of ammonium sulphate and of the rest, on the average the tenth part, had been transformed into hydrosulphate.

In solutions containing very large quantities of sulphate the ammonium phosphomolybdate could not be completely eliminated even when the acidulation of the liquid is conducted very cautiously, and the heating is continued very long. Here, however, the effects of heterostasis and of dissociation are accumulated.*

The relations are simpler with the borates. The separation of phosphomolybdate from solutions containing borates is completed when all the boric acid has been liberated by the nitric acid. This is proved by the following experiment.

A neutral solution containing 0·010 grm. P_2O_5 and 0·243 grm. MoO_3 along with ammonium nitric acid was further mixed with five grms. prismatic borax (*i.e.*, about 93 mols. $B_4O_7Na_2{}_{10}H_2O$ in reference to the mol. of phosphoric acid to be precipitated). In order to re-neutralise the liquid which had been rendered alkaline by the addition of borax, there were required (point not easily distinguished) about 1·50 grms. $NO_3H=170$ mols., and for precipitating the deposit altogether 1·90 grms. $NO_3H=214$ mols. If this number is reduced by the number of the mols. (23) required for converting

$$12MoO_4(NH_4)_2+PO_4H(NH_4)_2$$

into ammonium phosphomolybdate, there then remains

* The term "isostatic" can be applied to that form of combination of a body which involves the simultaneous existence of another body in such a manner that a change of the one involves a change of the other. In this sense the following compounds are isostatic with triammonium phosphododekamolybdic and with each other:—Ammonium hydrosulphate, ammonium hydrophosphate, monammonium-hexamolybdate, and boric acid. Isostasis exists also between triammonium heptamolybdate and triammonium-diphosphopentamolybdate. As heterostatic systems may be mentioned borax and nitric acid, which cannot coexist.

for the conversion of the borax into a condition isostatic with phosphomolybdate 191 mols.

A smaller quantity, 186 mols. NO_3H, is sufficient to liberate all the boric acid in the 93 mols. of borax.

6. *Action of Salts, of Water, and Acids upon Preformed Ammonium Phosphomolybdate.*

The action of the above-named compounds is very different according to the chemical nature of the bodies, and can be divided into the following three main groups.

1. Ammonium phosphomolybdate is not attacked either in cold or heat by ammonium chloride and nitrate unless the solution is too dilute and slightly acid.

In a perfectly neutral state the above salts do not dissolve any demonstrable quantities in the cold but they eliminate the two loosely combined equivalents of acid, so that the precipitate, after washing with the neutral saline solution, is saturated by 23 mols. of alkali like the phosphomolybdate dried at 150°. Probably in the combination the two mols. of acids which have been eliminated are replaced by as many mols. of neutral salt.

On prolonged heating with a perfectly neutral solution of ammonium nitrate or chloride a trace of the ammonium phosphomolybdate passes into solution and is again separated out by a trace of nitric acid. Perhaps this slight decomposition of the salt depends upon a partially retrograde reaction which tends towards the production of two mols. of nitric or hydrochloric acid, which then combines with the unchanged phosphomolybdate.

2. The ammonium phosphomolybdate is dissolved without the decomposition of the phosphomolybdic acid.

a. On account of a deficiency of ammonium salt in the solution, also by very dilute solutions of ammonium salt (less than 0·4—0·3 grm. NO_3NH_5 in 100 c.c.) on heating and by dilute acids, especially on prolonged heating. The solution in the two first cases are mostly turbid and milky, and can scarcely be clarified, and are yellowish, and on mixture with ammonium nitrate they re-deposit the phosphomolybdic acid which has been in solution.

b. In consequence of a transformation to soluble phosphomolybdate, on contact with sodium chloride or nitrate ammonium phosphomolybdate dissolves quickly, if heated, to a yellow solution of sodium phosphomolybdate, which forms a precipitate with ammonium salt. Chlorides and nitrates whose bases can form soluble phosphomolybdate act in a similar manner.

Potassium chloride and nitrate have only a slight action on account of the sparing solubility of potassium phosphomolybdate.

3. Ammonium phosphomolybdate dissolves with a more or less complete decomposition of the phosphomolybdic acid.

a. In consequence of an action which is tantamount to a partial saturation by alkali.

By heating with water considerable quantities of ammonium phosphomolybdate can be dissolved in a short time. The strongly acid solution, opalescent and more or less deeply yellow, according to the time of the action, is coloured a bright yellow on the addition of a few drops of nitric acid, and gives a strong precipitate with ammonium nitrate. Such a precipitate is produced by ammonium salt, even in a solution which has not been previously mixed with nitric acid. The filtrate, on the addition of a few drops of nitric acid, deposits a larger or smaller quantity of precipitate. The first precipitate, in proportion to the second, is the more abundant the longer the action of the water has lasted.

The salts of polybasic inorganic acids in degrees of saturation not isostatic with phosphomolybdate dissolve the yellow precipitate sparingly in the cold, but readily on heating, forming—even if the salt was neutral—colourless, strongly acid solutions, which, if mixed with nitric acid, re-constitute the yellow compound. Thus behave the neutral sulphates, phosphates, hydrophosphates, molybdates, &c.

The action of the salts of organic acids is quite analogous to that of free alkali. But, whilst the ammonium phosphomolybdate is completely separated out by nitric acid from the solutions of the salts of monobasic acids, provided there is a sufficiency of ammoniacal salt, and all the organic acid is set at liberty, the presence of polybasic acids, such as the oxalic and tartaric, prevents entirely the re-union of the elements of the phosphomolybdic acids, which appears from the fact that the colourless solution, on acidulation with nitric acid, neither gives a precipitate nor takes a yellow colour.

(To be continued).

THE MOLECULAR WEIGHTS OF CERTAIN SUBSTANCES AS INDICATED BY THE BOILING-POINTS OF THEIR SOLUTIONS.

By H. W. WILEY.

The apparatus with which the experiments to be described below were made was devised in August of this year, and the experiments were commenced about September 1. It was not my intention to publish the results of this work until they had been greatly extended, but the notice of the observations of Ernest Beckman of his employment of the same method induces me to submit the data already obtained for publication.

I have no desire whatever to question Mr. Beckman's priority in the use of the method, but it may be of interest to know that it was independently adopted by me, and all the data submitted below obtained before a notice of his work reached me in the *Chemisches Central-Blatt*, No. 7, 1889, this day received.

The apparatus employed consisted of an oval-round bottom flask of about 200 c.c. capacity, the neck of which was supplied with a side tube for the purpose of connecting it with an appropriate condenser. By this means the volume of the liquid employed was kept constant. The thermometer employed was accurately graduated to tenths, the distance between each tenth of a degree being so great that with the aid of the cathetometer used in reading it we could easily distinguish the 0·02 of a degree. The bulb of the thermometer was made to occupy the central portion of the liquid, the volume of which in all cases was 150 c.c. To protect the bulb of the thermometer against the influence of the steam bubbles it was covered with a double coating of fine copper foil. This method of coating the bulb of the thermometer of course precluded its use with substances easily reduced, such as silver and mercury salts.

Sodium chloride was the substance chosen to determine the factor for use. Carefully repeated determinations with this substance gave the following data:—

Substance taken	Sodium chloride.
Volume of water	150 c.c.
Weight of substance taken	4·5 grms.
Weight of substance taken to 100 c.c. of water	3·0 grms.
Boiling-point of water	99·47°
Boiling-point of sodium chloride in solution	99·93°
Total rise of temperature	0·46°
Rise of temperature for 1 grm. per 100 of substance..	0·1533°
Molecular weight of sodium chloride..	58·5

Factor = 0·1533 × 58·5 = 8·968.

Using this factor as a constant the accompanying determinations have been made (see Table, next page).

In addition to the numbers given above a large number of determinations have been made with substances containing water of crystallisation. In those cases the calculated molecular weight does not correspond either

Substance taken.	Volume water.	Wt. substance taken in grms.	Wt. substance taken in grms. to 100 c.c. water.	Temperature of boiling water.	Boiling temperature of substance in solution, °C.	Total rise of temperature, °C.	Calculated molecular weight.	Theoretical molecular weight.
KCl	150	6·0	4·0	99·50	99·85	0·35	76·91	74·5
KBr	150	6·0	4·0	99·50	99·79	0·29	123·7	119·0
KI	150	9·0	6·0	99·50	99·83	0·33	163·1	166·0
KNO_3	150	6·0	4·0	99·50	99 83	0·33	108·7	101·0
$K_2Cr_2O_7$	150	18·0	12·0	99·50	99·88	0·38	283·2	295·0
$NaNO_3$	150	6·0	4·0	99·44	99·86	0·42	85·4	85·0
Sucrose	150	20·0	13·33	99·50	99·70	0·20	643·2	342·0
Oxalic acid ..	150	6·0	4·0	99·50	99·70	0·20	179·4	90·0

with the theoretical molecular weight, including the water of crystallisation, nor with the molecular weight of the anhydrous salt. These results seem to indicate that substances containing water of crystallisation exist in solution in a modified form, and the influence of this modification on the boiling-point of the solution can only be determined by largely extended observations.

It is curious to note further that in the two organic substances examined the observed molecular weight obtained, using the same factor obtained by observations on the sodium chloride, is just about double the ordinary accepted molecular weight.

Since the factor for boiling solutions is so much less than that for the freezing mixtures, the determination of the molecular weight by the above method requires a solution considerably stronger than that used in Raoult's freezing method. The advantage, however, of having a mercurial column sensibly constant for long intervals of time renders it possible to make the observations with great accuracy.

To allow for the slight changes which take place in the boiling-point of water under the conditions mentioned, I propose, hereafter, to use two pieces of apparatus, one of which shall contain water to be kept constantly in use, the observation of the boiling-point of water and of the substance under examination being made at the same time. It is hardly necessary to mention that in such a case the thermometers employed would be carefully compared and the readings corrected accordingly. It is further necessary that the source of heat be sensibly constant, and we secure this by using a lamp with a certain sized flame which remains unchanged throughout the whole series of observations.

For assistance in the analytical data obtained I am indebted to Mr. W. H. Krug.

Sept. 14, 1889.

ON THE

COLOURS PRODUCED DURING THE TEMPERING OF STEEL.*

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It has long been observed, and every steel worker knows, that when bright steel is heated in the air to certain definite temperatures, a series of colours can be obtained, beginning with a light straw, and passing through a succession of brown and purple shades to a deep blue. These colours have attracted the attention of many observers, and suggest questions of interest as to the causes and circumstances of their production, and the physical and other problems therewith connected. In addition, however, to any other cause of interest these colours possess, they have been studied on account of their real and supposed importance in the arts. Everyone must be familiar with the different shades of colour which are given to steel pens, varying from a very light straw to a deep purple or blue. These various shades are commonly produced by heating the clean bright pens, in their otherwise finished condition, to a suitable temperature in a revolving cylinder. When the desired colour has been obtained the pens are immediately cooled by being turned quickly out on to a sieve or other cooling place, so that the colour produced may not change by further heating. The colours of the pens met with in commerce are, however, not quite the same as those produced as above described, since the tints are slightly altered by the lacquer which is used to prevent rusting. Another well-known application of these colours is in the ordinary method of tempering steel, which is a very important, though, in many cases, an extremely delicate operation. After the steel has been hardened, say, in the form of a plain drill or chisel or other simple tool, the workman commonly cleans a portion of the surface of the steel, and then once more cautiously heats it until a certain desired colour is obtained on the bright surface; the tool is then usually immediately cooled in water. It will be seen, therefore, that the formation of a particular colour is assumed to correspond more or less nearly with a certain combination of hardness and tenacity which is required in the tool, and when it is remembered that usually the value of the tool is dependent to a very considerable extent on the temper which is imparted to it, and that the workman judges of this temper by the colour of the surface, it will be seen that the study of the properties of these colours is of great importance to thousands of workshops in this country. Further, the whole range of temperature used in tempering steel generally extends only from about 220° to 320° C., or thereabouts, that is, only about 100° C. (though we have good reason to believe that this range is capable of extension); it will be seen, therefore, that it must involve very considerable experience to successfully temper a piece of steel when the operator is obliged to work in the manner above described.

Thus, within the range of only one hundred degrees Centigrade, we have compressed the points which are necessary for the proper treatment of a knife-edge and a cold chisel, a razor and a spring, a steel engraver's tool and a saw, a lancet and a hatchet, tools as opposite as possible in properties and uses, and each and all of which would be entirely unfitted for their purpose if treated improperly during tempering. It is no exaggeration to say that a difference of only ten degrees Centigrade would often exert a considerable influence on the usefulness of a tool, and yet in most cases the workman can only judge of the temperature employed by the colour he observes. How far this is a trustworthy guide we shall consider anon, but it is of interest to notice that almost exactly a century ago, on June 9, 1789, a patent (1687) was granted to David Hartley for the use of a "pyrometer or thermometer, or other precise or regulated mode of measuring heat in tempering articles made of steel, instead of the mode hitherto accustomed of tempering them by colour," and Hartley stated that usually the tempering heats "lie between the points of four hundred and six hundred degrees upon Fahrenheit's scale of heat." For delicate work the thermometer has been more or less in use ever since Hartley's time.

Several writers (including Aikins, Jeans, and others) have attributed the use of a fusible metal bath, and the

* A Paper read before the Birmingham Philosophical Society, June 13, 1889.

determination of colour temperatures, as now generally received, to Hartley. Certainly, fusible metal and other baths were used early in the present century (see Aikins' "Chem. Dict.," 1807, vol. i., p. 604), but I have not been able to establish any connection between these and Hartley, whose patent above quoted gives most general directions for applying heat, evidently without later refinements, and gives no more details of temperature than above quoted. The best and most complete colour-tempering scale with which I am acquainted was published in the form of a coloured diagram with the "Report of the United States Chief of Ordnance," 1885, p. 204.

Most writers who touch on this subject treat it in a stereotyped manner, stating that when bright steel is heated to a certain temperature, such and such a colour is produced, and this is suitable for lancets, chisels, springs, or other articles, as the case may be. It is, therefore, tacitly assumed, though not perhaps actually stated, that a particular colour corresponds to a certain temper, and is invariably produced at a particular temperature. In fact, the three things—colour, temper, and temperature—might, so far as the text-books are concerned, be closely and for ever united.

The cause of the production of these colours is now universally, I believe, acknowledged to be the formation of thin films of oxide on the surface of the metal when it is heated in presence of air. Even this question was at one time in dispute, such men as Davy ("Chemical Phil.," p. 390) and Thomson ("Chemistry," vol. i., p. 224) taking the opposite view. But Davy afterwards showed ("Thomson's Annals," 1813, vol. i., p. 131) that steel might be heated in a neutral gas, such as hydrogen or nitrogen, without being coloured on its surface, and that steel remained colourless when heated under the surface of oil or of mercury.* I have frequently heated bright strips of polished steel for hours under the surface of mercury or oil without discolouration, while they would have been instantly coloured at the temperature used if heated in contact with air. I think, further, that there can be little doubt that the oxide so produced is practically transparent, first, because the sequence of colours is what would be expected in films of a transparent substance when the thickness of the films gradually increases; also because of observations on the reflected light, the colour of which varies somewhat at different angles; but chiefly because it is found that on increasing the temperature a little above the point necessary to produce a dark blue, the colour gradually disappears (though doubtless oxidation proceeds more rapidly), and the surface, though covered with more oxide, becomes almost colourless again.

When it is granted that the colours we are considering are the result of oxidation, it would at once appear probable that the nature of the surface to be heated, its freedom from dirt and grease, and the length of time during which it is heated, would all exert a considerable influence on the shade produced. It would also appear probable that the amount of carbon present in the metal, and the condition in which the carbon existed, would have comparatively little influence. Hitherto my experiments have been chiefly directed to the study of these simple and, as they appear, almost self-evident conclusions.

Heating has usually been performed in a large air oven, inside of which, about two inches from the bottom, was an iron tray, supported on fire bricks, and filled with sand to the depth of about an inch, a small space being left all round the tray so as to prevent contact with the sides of the oven. Resting on the surface of the sand, but not touching the edges of the tray, was a plate of copper, on which were placed the strips of steel it was desired to heat. The object of this arrangement was to prevent irregular heating from below, and to give as much uniformity as possible. Passing through the centre of the copper plate, and partly covered by the sand, was the thermometer used; and, as even with these precautions it was not found possible to get perfect uniformity, a considerable number of strips was operated upon at one time, and about four removed, from different parts of the plate, when an observation was made. I am indebted to Messrs. Perry and Company, Limited (late Sir Josiah Mason) for specimens of bright crucible pen steel, both in the soft and in the hardened condition, while Mr. G. H. Strick, of Brynamman, kindly supplied me with samples of bright wrought-iron.

It is, of course, necessary that for such experiments the steel to be used should be clean and bright. A rough surface does not give nearly the same brilliancy of colour as is noticed when the metal is carefully polished, though the shade is pretty nearly the same in both cases. The presence of dirt usually causes irregular colouring, producing bands or spots of colour different to the rest of the surface. Naturally, too, some kinds of dirt appear to assist oxidation, though the shade is less brilliant, while other kinds of dirt exert a protective influence. The brightest shades are produced with perfectly clean and polished surfaces, and few people are aware of the gorgeousness of the shades of purple and blue which can be produced on a large surface with proper conditions.

In connection with the supposed relationship between colour and temper, I have taken strips of bright steel, hardened and unhardened, and also bright wrought-iron, and heated them as above described at various temperatures, for definite periods, and find that practically each of these three varieties of iron gives the same colours in the same time. The only difference I have been able to perceive is that the hardened steel gives the brightest colour, and the wrought iron the least brilliant. This difference in brilliancy is, no doubt, due to the fact that the surface was more perfect in the hardened steel specimens, which had been carefully cleaned by rotation with sand in barrels for a lengthened period. The fact that in each of the three cases the shade produced under similar circumstances is identical shows at once that the colour on a steel tool is no indication whatever as to the content of carbon or the temper of the steel.

As bearing on this aspect of the question it may be mentioned that Bousfield patented (1866, No. 2810) a method of blueing the surface of sheet iron. After the sheets had been properly cleansed they were heated in an air-tight flask for a good many hours at 700° F., care being taken that no two sheets were in contact with each other. Probably a lower temperature and a shorter time, with free access of air, would produce a similar result. I notice, too, that in some cases cast-iron is coloured in a similar manner, and this fact confirms the above conclusions.*

From the very beginning of my experiments I have been struck with the fact that *time* has a most important influence in developing these colours. From a study of ordinary text-books one might readily conclude that to produce a light straw colour about 221° C. is necessary, while about 320° C. is required to produce a blue colour. Such a conclusion would, however, be quite erroneous, for it is easy, by heating the specimens for a comparatively lengthened period, to produce a *blue* colour at a temperature *below* that which is usually regarded as necessary to give a *straw colour*, or over 100° below that which is generally accepted as producing a blue. In the same way a straw colour can be produced, in a few minutes, fully 50° below 221° C., which is the generally accepted temperature. It will be found, however, that, as we pass from shade to shade up the series, each colour requires a longer interval for its production at a given temperature than the one which preceded it. Thus, at a

* Professor Roberts-Austen has also shown that steel is not coloured when heated in vacuo (Inst. M. E., 1881, p. 710).

* Dr. Percy has given details of the methods used to obtain the bright grey-black coating on Russian sheet-iron. "Manufacture of Russian Sheet-iron, 1871." The colour in this instance is partly due to carbonaceous matter.

given temperature, we may pass from very light straw to straw, a well-marked change, in a few minutes, while at the same temperature it may require almost as many hours to pass from purple to blue. Further, in starting with low temperatures, the intervals of time between the various shades are greater, and becomes very considerable indeed for the deeper shades. For example, a purple can be produced at 250° in a few minutes which would require an hour at 220°, or about twelve hours at 170°, though the ultimate result would be the same in each case.

On the other hand, it can be shown that, with a deficiency of oxygen, iron or steel may be heated far above the temperatures previously mentioned without producing the usual succession of colours. Thus, in annealing sheet-iron in the manufacture of tin plates, a number of sheets are heated to redness for some hours in an iron box, from which the air is excluded as far as possible. On removing the sheets when cold they are found to be straw-coloured or brown in the centre over perhaps two-thirds of their area. Surrounding this centre portion, passing outwards in order, are found purple, blue, light blue, blue green, and nearly colourless, depending on the amount of oxidation, though the sheets themselves have been exposed for a considerable time to a red heat. Bousfield's patent, above mentioned, is another example of the same kind.

Details of a few of my own experiments, undertaken to try and determine the interval between definite shades, may serve to illustrate these facts. Thus:—

Total Time of Heating at 221°—227° C.	Interval between Samples.	Colour.
5 mins.		Dark straw.
12 ,,	7 mins.	Brown.
21 ,,	9 ,,	Brown, with purple.
32 ,,	11 ,,	Nearly all purple.
45 ,,	13 ,,	Purple, with some blue spots.
60 ,,	15 ,,	Very similar.
77 ,,	17 ,,	Nearly all blue.
95 ,,	19 ,,	Very similar.
117 ,,	21 ,,	Deep blue.
140 ,,	23 ,,	Blue, with a slight tinge of green.

It will be seen, on examination of the specimens shown that several of the above colours are "bastards," *i.e.*, transition-colours, and that although the last interval (twenty-three minutes) is more than four times as long as the first (five minutes), still the early intervals are too long, and the later ones too short. Another experiment gave:—

Total Time of Heating at 220°—227° C.	Interval between Samples.	Colour.
1 min.		Very light straw.
4 ,,	3 mins.	Light straw.
9 ,,	5 ,,	Straw.
16 ,,	7 ,,	Brown.
25 ,,	9 ,,	Brown, with purple.
36 ,,	11 ,,	Brown and purple, about equal.
49 ,,	13 ,,	Purple, with some brown.
64 ,,	15 ,,	Purple, with blue.
81 ,,	17 ,,	Nearly all blue.
100 ,,	19 ,,	Blue.

In this experiment, though the time of heating varied the squares of the numbers from one to ten, still the intervals were too short in the later samples, and transition colours were obtained. The earlier samples, also, were not so definite as might be desired, though it would be difficult to express the slight variations in words. The following was a more successful experiment:—

Total Time of Heating at 220°—227° C.	Interval between Samples.	Colour.
2 mins.		Very light straw.
4 ,,	2 mins.	Straw.
8 ,,	4 ,,	Dark straw.
16 ,,	8 ,,	Brown.
32 ,,	16 ,,	Brown, with purple.
64 ,,	32 ,,	Purple.
128 ,,	64 ,,	Dark blue.
256 ,,	128 ,,	Greenish blue.

The three series of steel test pieces, as above, are exhibited in the room, and it is evident to all that the last of the three experiments gave far the best results, as judged by the distinctness of the shades produced. Hence at the temperature used (220°—227° C., corresponding closely with 221°, commonly accepted as giving a straw colour), the time required to pass from one distinct shade or colour to the next increases approximately in geometrical progression. Dr. Poynting has suggested that at the temperatures used in my experiments the film of oxide first formed may act as a protection to the surface of the metal, and that the rate at which the thickness of the film increases may be represented by a logarithmic curve. I do not venture to suggest that a similar rule would hold good for all temperatures, of that I have no evidence; but this is certain, that at low temperatures, such as, say, 150°, the various colours can be produced, but it requires very prolonged heating in order to obtain the blue shades. On the other hand, the lighter colours can be produced at a high temperature, but require very little time for their development. I have not attempted to determine the lowest temperature at which these colours can be produced, and should imagine it would be difficult to do so accurately. I have, however, succeeded very well at 150°—160° C., and do not doubt that with sufficient time a still lower temperature will suffice.

Though the foregoing observations prove that the colour developed is dependent as much upon time as upon temperature, and that the colour is independent alike of the amount and the condition of the carbon present, so long as the surfaces and other conditions are alike; still these observations merely suggest another and more important question, namely, how far the temper of the steel may be affected, and its properties changed, by continued heating at a temperature below that which is generally employed for tempering. Hitherto I have not been able to obtain quantitative results in this connection, owing to the fact that steel strips, even when carefully hardened, not only differ in the various pieces, though cut off the same sheet and treated in the same manner, but even the same strip will very commonly differ in hardness on the two sides, and not unfrequently, even in a strip of only some three inches in length, one side of the strip will be different at each end, while the middle will not agree with either. Hence some more satisfactory method of experiment is required; but in the meantime I have satisfied myself that hardened steel strips, if heated for some hours at 220° C., are distinctly softer than similar strips which have been heated for a shorter time; and that, though a few minutes at 220° produces a distinct effect, the interval has to be considerably increased from time to time in order to produce further and further appreciable softening of the steel.

I am informed that the experience of steel pen manufacturers lends support to the above opinions, and I may venture, in conclusion, to refer to other observations in the same direction. Brande ("Chemistry," 1848, vol. i., p. 759) gives the following interesting details in reference to the preparation of knife-edges for a pendulum used by Capt. Kater (*Phil. Transactions*, 1818, p. 38), the details of which preparation were not given in Capt. Kater's original paper. Brande states that the knife edges "were

forged by Mr. Stodart from a piece of fine wootz; they were carefully hardened and tempered in the bath at 430° F.; on trial they were found too soft. They were a second time hardened, and then heated to 212°. The intention was to increase the heat from that point, trying the temper at the advance of about every 10°. In the present instance this was not necessary, the heat of boiling water proving to be the exact point at which the knife-edges were admirably tempered." "It is highly probable," Brande continues, "that steel for many uses may be sufficiently tempered in a range so extensive as from 212° to 430° (100° to 221° C.). But it is *not the temperature only, but also the time during which the steel is exposed to it*, which influences its hardness or temper." The italics in the above quotation are mine.

As confirming the view that steel may be tempered at at a lower temperature than is usually supposed, there are also the experiments of Professor Langley (Inst. M. E., 1882, p. 148), who showed that the density of steel was distinctly reduced (*i.e.*, the steel was hardened) by cooling rapidly from the boiling point of an alkaline solution used for removing the scale from the specimens examined. So far as my observations have gone I believe—

1. In the words of Brande:—"It is not the temperature only, but also the time during which the steel is exposed to it, which influences its hardness or temper."

2. High carbon steels are more sensitive to the effects of comparatively low temperatures than are steels containing less carbon.

3. The colours observed in tempering steel can be produced by suitably varying the conditions, at temperatures far either above or below those usually accepted as necessary to produce a particular shade; the colours can be produced alike with hardened or with unhardened steel; and with wrought-iron or cast-iron as well as with steel. They are, therefore, independent of the amount or condition of the carbon present in the steel.—*Proceedings of the Birmingham Philosophical Society*, Vol. vi., Part 2.

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

(Continued from p. 184).

Problem XI. *To Determine whether Oxides such as Water and Chalk Gas may be Deprived of Oxygen by means of Metals.*—It being found that hydrogen and carbon withdraw the oxygen from some but not from all metals, it follows that some metals have a stronger, others a weaker, hold upon or "affinity" to oxygen than has either oxygen or carbon; the question arises whether any and which metals have so much greater an affinity to oxygen that they will withdraw it from hydrogen and carbon. Copper and iron have been found to part with oxygen, but zinc and magnesium did not; so these four metals may be studied comparatively. Steam is passed through a red-hot copper tube full of copper tacks: no change is observed. The experiment is repeated with an iron tube charged with bright iron nails: a gas is obtained which is soon recognised to be hydrogen, and on emptying out the nails they are found to be coated with black scale. Zinc and then magnesium are tried, and, like iron, are found to liberate hydrogen. Chalk gas is next passed over red-hot copper, and is found to remain unchanged, but on passing it over red-hot iron or zinc a gas is obtained which burns with a clear blue smokeless flame: this gas is not absorbed by milk of lime, but on combustion yields chalk gas, so it evidently contains carbon, and is a new combustible gas. Like hydrogen it is found to afford an explosive mixture with oxygen. Finally, magnesium is heated in chalk gas: it is observed to burn, and the magnesium to become converted into a blackish substance unlike the white oxide formed on burning it in air. But it is to be expected that this oxide is produced, and to remove it, as it is known from previous experiments to be soluble in muriatic acid, this acid is added: a black residue is obtained. What is this? Is it not probable that it is carbon? If so, it will burn in oxygen yielding chalk gas. So the experiment is made. These experiments in which hydrogen is obtained from water and carbon from chalk gas afford the most complete "analytic" proof of the correctness of the conclusions previously arrived at regarding water and chalk gas, and which were based on "synthetic" evidence; taken together, they illustrate very clearly the two methods by which chemists determine composition.

As hydrogen and carbon form oxides from which oxygen may be removed by means of some metals, but not by all, the question arises, which has the greater hold upon or affinity to oxygen—carbon or hydrogen? As it is the easiest experiment to perform, steam is passed over red-hot charcoal: a combustible gas is obtained which yields water and chalk gas when burnt, so evidently the hydrogen is deprived of its oxygen, and this latter combines with the carbon, forming the combustible oxide of carbon. Will not carbon partly deprive chalk gas of its oxygen? The experiment is made and it is found that it will. These results afford an opportunity of calling attention to and explaining the changes which go on in ordinary fires and in a furnace.

Problem XII. *To Determine the Composition of Salt Gas, and the Manner in which it Acts on Metals and Oxides.*—It has previously been demonstrated that spirits of salt or muriatic acid is prepared by acting on salt with oil of vitriol and passing the gas which is given off into water; the solution has been found capable of dissolving various metals and oxides, chalk, lime, &c., and as water alone does not dissolve these substances the effect is apparently attributable to the dissolved gas, so it becomes of interest to learn more of this gas in order that its action may be understood. It is first prepared; its extreme solubility in water is observed, and also the fact that as it dissolves much heat is given out; and it is noted that although colourless and transparent it fumes in the air. How is its composition to be determined? Is there any clue which can be followed up? Reference is made to the previous observations, and it is noted that its solution dissolves various metals with evolution of hydrogen; water alone has no such effect. Is this hydrogen derived from the water or from the dissolved gas? The gas alone is passed over heated iron-turnings, and the escaping gas is collected over water; it proves to be hydrogen, so evidently salt gas is a compound of hydrogen with something else. How is this something else to be separated from the hydrogen? Do not previous experiments suggest a method? Yes, they have proved that hydrogen has a marked affinity to oxygen, and now it is recollected that on treating muriatic acid with red lead—a substance rich in oxygen—a greenish yellow gas is obtained. The experiment is repeated on a larger scale and the gas is examined. If it is contained together with hydrogen in salt gas, perhaps salt gas will be obtained on applying a flame to a mixture of the two gases just as water is from a mixture of oxygen and hydrogen: the mixture is made and fired, and the result leaves little doubt that salt ga does consist of hydrogen in combination with the greenish yellow gas—chlorine. Whence is this chlorine derived—from the salt or the sulphuric acid?

The notes are again consulted, and it is seen that a solution of silver in nitric acid gave a characteristic precipitate with muriatic acid but not with sulphuric, so salt solution is added to the silver solution, and a precisely

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe. Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

similar precipitate is obtained, leaving little doubt that the chlorine is derived from the salt. It is now easily realised that the iron and zinc displace the hydrogen of the dissolved hydrogen chloride. What happens when the oxides are acted on? In addition to the metal they contain oxygen, which is known to combine readily with hydrogen, forming water; is water formed? Lime oxide is therefore heated in hydrogen chloride; a liquid is obtained which behaves exactly as a solution of hydrogen chloride in water. When the action is complete, after driving off all that is volatile, a solid remains very like fused common salt—doubtless zinc chloride, as it is to be supposed that as the hydrogen has taken the place of the zinc the chlorine has taken the place of the oxygen. What, then, is the action of hydrogen chloride on chalk? It evidently not only separates the chalk gas from the lime, but also dissolves this latter. What is formed? Dry (unslaked) lime is therefore heated in a current of hydrogen chloride. It behaves just as zinc oxide, yielding a liquid product—evidently a solution of hydrogen chloride in water, as it dissolves zinc with evolution of hydrogen, and the residue is like that of zinc chloride. The important discovery is thus made that lime also is an oxide—that chalk, in fact, is a compound of two oxides; the resemblance of lime to zinc oxide and magnesium oxide is so striking that the conclusion is almost self-evident that lime is probably a metallic oxide, and it may be here pointed out that this actually is the case. The gradual discovery of the composition of chalk in the manner indicated is an especially valuable illustration of chemical method, and serves to show how chemists are often obliged to pause in their discoveries and to await the discovery of new facts and methods of attack before they are able to attack before they are able to completely solve many of the problems which are submitted to them. The solids obtained on dissolving zinc oxide and lime in muriatic acid and boiling down the solution, when all the water is driven off, are white solids like fused salt, but on exposure they gradually become liquid. In so doing they increase in weight, and evidently behave like sulphuric acid. Probably water is absorbed from the air: no change takes place when they are kept over sulphuric acid or dry lime. In this way two new desiccating agents are incidentally discovered.

Problem XIII. *To Determine the Composition of Washing Soda.*—The study of this substance is of importance as introducing the conception of an alkali. The preparation from salt is first described. On heating the crystals they melt and give off "steam"; the experiment is made in such a way that a quantity of the liquid is obtained sufficient to place beyond doubt that it is water. The water is found to be easily driven off on heating the crystals in the oven, and to constitute a very large proportion of the weight of the crystals. The conception of water of crystallisation is thus gained. On heating the dried substance to full redness in the platinum dish, no loss occurs. The residue dissolves in water, and "soda crystals" may again be obtained from the solution, so that heat does not affect it. Perhaps acids which have been found to act so powerfully in other cases will afford some clue—on trial this is found to be the case: a colourless odourless gas is given off, which extinguishes a burning taper. Is this perhaps nitrogen or chalk gas? The lime water test at once decides that it is the latter. So it is determined that washing soda, like chalk, is a compound of chalk gas—but with what? With an oxide? The dried substance is heated in hydrogen chloride: chalk gas is given off as before, and a liquid which is soon recognised as water saturated with hydrogen chloride. The residue dissolves in water, and separates from the concentrated solution in crystals exactly like salt, and, in fact, is soon recognised to be salt; evidently, therefore, that which is present in salt along with chlorine is present in soda crystals along with oxygen, chalk gas, and water. The preparation of the metal sodium from soda is then explained. Acquaintance being thus made with compounds of chalk gas with two different oxides, the question arises, which oxide has the greater affinity to the chalk gas? Will lime displace sodium oxide from soda or *vice versâ?* On adding lime water to soda solution a precipitate of chalk is formed. What does the solution contain? Lime water contains lime in combination with water; is the sodium oxide present in combination with water? Soda is boiled with milk of lime (in an iron saucepan to avoid breakage) until it no longer affects lime water; afterwards the liquid is poured off and boiled down. The product is very unlike soda: it is very caustic, and when exposed to the air becomes liquid. If it is an analogous substance to slaked lime, it should combine with chalk gas and be reconverted into soda; this is found to be the case. Caustic soda is thus discovered. Chalk and lime are known to neutralise acids; both soda and caustic soda are found to do so, and their effect on vegetable colours is found to be the reverse of that of acids. At this stage the origin of the name alkali is explained, and it is pointed out that the oxides which have been studied may be arranged in two groups of alkali-like or *alkylic* and acid-forming or *acidic* oxides, the former being derived from metals, the latter from non-metals. The production of *salts* by the union of an oxide of the one class with the oxide of the other class is then illustrated by reference to earlier experiments.

The point is now reached at which the results thus far obtained may be reconsidered. The student has been led in many cases to make discoveries precisely in the manner in which they were originally made; and it is desirable that at this stage, if not earlier, the history of the discovery of the composition of air and water, &c., should be briefly recited. It is then pointed out that a variety of substances have been analysed and resolved into simpler substances—air into oxygen and nitrogen, water into oxygen and hydrogen, &c.; and that these simpler substances thus far have resisted all attempts to further simplify them, and are hence regarded as elements. A list of the known elements having been given, the diverse properties of the elements may be illustrated from the knowledge gained in the course of the experiments. The fact that when elements combine compounds altogether different in properties from the constituents are formed also meets with manifold illustration. Too little has been ascertained to admit of any general conclusion being arrived at with regard to the proportions in which elements combine, but it clear that they may combine in more than one proportion since two oxides of carbon have been discovered, and in the only cases studied — viz., copper oxide and chalk—the composition has been found not to vary. The existence of various types of compounds has been recognised, and a good deal has been learnt with reference to the nature of chemical change. But, above all, the method of arriving at a knowledge of facts has been illustrated time after time in such a manner as to influence in a most important degree the habit of mind of the careful student. New facts have been discovered by the logical application of previously discovered facts: the logical use of facts, and the habit of using facts have been inculcated. This is all-important. It has become so customary to teach the facts without teaching how they have been discovered that the great majority of chemical students never truly learn the use of facts; they consequently pursue their daily avocations in a perfunctory manner, and only in exceptional cases manifest those qualities which are required of the investigator; their enthusiasm is not awakened, and they have little desire or inclination to add to the stock of facts. It must not for one moment be supposed that the object of teaching chemistry in schools is to make all chemists. Habits of regulated inquisitiveness, such as must gradually be acquired by all who intelligently follow a course such as has been sketched out, are, however, of value in every walk of life; and certainly the desire to understand all that comes under observation should as far as possible be implanted in everyone.

STAGE V.—*The Quantitative Stage.*

The *quantitative* composition of many of the substances which have previously been studied qualitatively should now be determined—in some cases by the teacher in face of the pupils, so that every detail may be odserved and all the results recorded; in other cases by the pupils.

The composition of water is first determined by Dumas's method; this may easily be done, and fairly accurate results may be obtained in the course of a couple of hours. The results obtained by Dumas and subsequent workers should then all be cited, and, attention having been drawn to the extent to which such experiments are necessarily subject to error, the evidence which the results afford that hydrogen and oxygen combine in certain *fixed and invariable proportions* to form water is especially insisted upon.

The composition of chalk gas is next determined; this also is easily done, as impure carbon (lampblack) may be burnt and the hydrogen allowed for. Again, attention is directed to the results obtained by skilled workers, and the evidence which they afford that chalk gas never varies in composition.

The composition of copper oxide has already been ascertained; it may be re-determined by reducing the oxide in hydrogen: in fact, in determining the composition of water.

The lead oxides may be reduced in a similar manner, the oxide obtained by igniting white lead as well as red lead and the brown oxide obtained by treating red lead with nitric acid being used. In this way it is ascertained that the brown oxide is the highest oxide; the loss in weight which this oxide suffers when ignited may then be determined.

Tabulating the results thus obtained, after calculating with what amount of the particular element that quantity of oxygen is associated which in water is combined with one part by weight (*unit weight*) of hydrogen, numbers such as the following are obtained:—

Parts.			Parts.		
1	hydrogen is combined	with	8	oxygen	in water
3	carbon	,,	8	,,	chalk gas
31·5	copper	,,	8	,,	copper oxide
103·5	lead	,,	8	,,	lead oxide (litharge)
51·8	,,	,,	8	,,	lead oxide (brown).

These clearly illustrate the fact that elements combine in very different proportions, and the results obtained with the lead oxides afford also an illustration of combination in multiple proportion.

The amounts of silver and lead nitrates formed on dissolving silver and lead in nitric acid are next determined by evaporating the solutions of known weights of the metals in porcelain crucibles on the water-bath, and then drying until the weight is constant; accurate results may be easily obtained, and these two exercises afford most valuable training. The nitrates are subsequently evaporated with muriatic acid and the weights of the products determined. What are these products? Does the metal simply take the place of the hydrogen in hydrogen chloride as zinc does when it dissolves in muriatic acid? If so, the products are silver and lead chlorides, and it may be expected that the same substances will be obtained—that the same increase in weight will be observed, when, say, silver is combined directly with chlorine as when it is dissolved in nitric acid and the solution is precipitated with muriatic acid or salt. Silver is, therefore, heated in chlorine, and is found to increase in weight to the same extent as when it is dissolved in nitric acid, &c.; a given weight of silver precipitated by salt is also found to increase to the same extent as when it is directly combined with chlorine. The composition of silver chloride having thus been ascertained, the amount of chlorine in salt is determined. The composition of salt being ascertained, purified dried washing soda is converted into salt, and also the amount of chalk gas which it contains is determined: from the data, the composition of sodium oxide may be calculated. In like manner the composition of lime may be ascertained by converting chalk into chloride, by igniting it in hydrogen chloride, and then determining the chlorine in the chloride; the same method may be applied to the determination of the composition of the oxides and chlorides of zinc, magnesium, and copper.

Discussing these various results, and comparing the quantities of oxygen and of chlorine which combine with any one of the metals examined, it is seen that in every case about 35·4 parts of chlorine takes the place of eight parts of oxygen. Combination in *reciprocal proportions* is thus illustrated, and by considering the composition of chalk and washing soda it may be shown that this applies equally to compounds of two and to compounds of three elements. As 35·4 parts of chlorine is found in every case to correspond to eight parts of oxygen, it is to be expected that hydrogen chloride contains one part of hydrogen in combination with 35·4 parts of chlorine; a solution containing a known weight of hydrogen chloride is, therefore, prepared by passing the gas into a tared flask containing water, and the chlorine is then determined.

It being thus clearly established what are *equivalent* weights of elements, the conception of equivalents may be further developed by exercises in acidimetry carried out by the pupils themselves. The proportions in which washing soda and hydrogen chloride interact may be determined by mixing solutions of known strength until neutralisation is effected; if the solution be evaporated and the chloride weighed, the results may be used in calculating the composition of hydrogen chloride; they serve, in fact, as a check on the conclusions previously arrived at as to the composition of washing soda and hydrogen chloride. Solutions of sulphuric and nitric acid may be similarly neutralised, and, the amounts of sulphate and nitrate formed having been ascertained, the equivalents of the acids may be calculated on the assumption that the action is of the same kind as takes place in the case of hydrogen chloride. Determinations of the strengths of acids, &c., may then be made. In a similar manner the volumetric estimation of silver may be taught and the percentage of silver in coinage and other alloys determined.

Such a series of quantitative exercises as the foregoing, when carried out *before* and to a considerable extent *by* the pupils, undoubtedly affords mental discipline of the very highest order, and is effective of good in so many ways that the value of such teaching cannot be overestimated. The failure to grasp quantitative relationships which examiners have so frequently to deplore is without question largely, if not alone, due to students' entire ignorance of the manner in which such relationships have been determined. Moreover, the appreciation by the general public of the principles on which quantitative analysis is founded would undoubtedly be directly productive of good in a multiplicity of cases.

STAGE VI.—*Studies of the Physical Properties of Gases in Comparison with those of Liquids and Solids. The Molecular and Atomic Theories and their Application.*

A series of quantitative experiments on the effect of heat on solids, liquids, and gases should now be made, and these should be followed by similar experiments on the effect of pressure: the similar behaviour of gases, and the dissimilar behaviour of liquids and solids, is thus made clear. The condensation of gases is then demonstrated and explained, and also the conversion of solids and liquids into gases, and the dependence of boiling-point on pressure and temperature. Regnault's method of determining gaseous densities is studied, and the method of determining vapour densities is illustrated. The molecular constitution of a gas is now discussed; the phenomena of gaseous and liquid diffusion are studied

and a brief reference is made to the kinetic theory of gases; then Avogadro's theorem is expounded and applied to the determination of molecular weights; and eventually the atomic theory is explained, and the manner in which atomic weights are ascertained is brought home to the pupils. The use of symbols must then be taught. Finally, the classification of the elements in accordance with the periodic law should be explained.

It is all-important that at least a large proportion of the experiments in each of the stages should be made by the pupils; but even if this were not done and the lessons took the form of demonstrations, much valuable instruction might still be given.

The majority of pupils probably would not proceed to the fifth and sixth stages; but those who perforce must terminate their studies without gaining any knowledge of chemical philosophy should unfailingly be led to make a few simple quantitative experiments: for example, to determine silver volumetrically, and the method of determining the composition of water and chalk gas should be demonstrated in their presence: and it may be added that if only the examples in Stages I. and II. and Problems I. to V. of Stage III. were thoroughly worked out, most important educational training would be given and much valuable information as to the nature of common phenomena would be gained.

The complete course would undoubtedly take up considerable time, but so does a satisfactory mathematical or classical course of study, and it is absurd to suppose that useful training in science is to be imparted in a few months. If instruction be given in the manner suggested at all generally, it will be necessary, however, to modify the present system of testing results. Pupils could not be expected to pass at an early age examinations such as are at present held, and awards would have to be based chiefly on an inspection of the classes at work, and of note-books, and on *vivâ voce* questioning. But all are agreed that the present system of payment on results tested by a terminal examination is a most unhealthy one, and that a more rational system *must* be substituted for it. I may suggest that if members of the staff of science colleges, such as are now established in so many towns, could be appointed *supervising inspectors*, whose duty it would be to advise teachers in schools and *occasionally* to inspect the teaching in company with the permanent inspector, it would be possible to secure the assistance of a body of men who are in touch with scientific progress and conversant with the improvements which are being effected. A man who "once an inspector is always an inspector" of necessity must get into a rut, and will escape from the wholesome leavening and rousing influence which is always more or less felt by those whose office it is to follow the march of scientific progress.

It should also here be pointed out that the great majority of the experiments and exercises described may be carried out with very simple apparatus and with slight provision in the way of special laboratory accommodation. In but very few cases is there any production of unpleasant smells or noxious fumes. It is, in fact, a mistake to suppose that an elaborately fitted laboratory is in every case essential for successful teaching: much might be done in an ordinary schoolroom provided with a demonstration bench for the use of the teacher, a draught closet over the fire-place, a sink, a raised table for balances (raised so that the teacher might see what was going on), a cupboard for apparatus, and a long narrow bench provided with gas burners at which, say, twenty pupils might stand ten a side. At present the Science and Art Department will not recognise "practical chemistry" unless it be taught in a laboratory fitted up in a certain specified manner, and their regulations are such as to enforce the provision of expensive laboratories in all cases where it is desired to obtain the grant. If greater latitude in fittings were allowed, more attention being paid to the character of the work done and less to the tools with which it is accomplished, probably much less money would be wasted by inexperienced school authorities in providing special laboratories, and there would be much greater readiness displayed to enter on the teaching of experimental science. The course which has been sketched out is one which doubtless might well be modified in a variety of ways according to circumstances. Thus many simple exercises in mechanics, in addition to those directly mentioned, might be introduced into Stage II., and the mechanical properties of common materials might be somewhat fully studied at this stage in districts where engineering trades are largely established, and where such knowledge would be specially valuable. In like manner the physical effects of heat on substances might be studied in Stage III. instead of Stage VI. And there are other chemical problems and simple exercises besides those described which might be substituted for some of them or included in the course.

Probably, however, it would be found undesirable, if not impossible, as a rule, to continue the teaching of chemistry proper much, if at all, beyond the stage indicated in this scheme. Other subjects will have a prior claim should it ever be deemed essential to include in a comprehensive scheme of school education the elements of the chief physical and physiological sciences; it certainly is of primary importance to introduce at as early a period as possible the conception of energy, and to explain the mechanical theory of heat, so that later on it may be possible to discuss the efficiency of heat and other engines; and, until the laws of the electric current are understood, the subject of chemical change can never be properly considered.

In many cases, where it is convenient or desirable to continue the chemical studies, it probably will be advantageous as a rule that they have reference to specific (local) requirements—*e.g.*, to agriculture in schools in agricultural districts; to food materials and physiology in the case of girls especially, &c. But in any case more consideration must be paid in the future in schools where chemistry is taught to educational requirements—the teaching must have reference to the requirements of the general public; and it must be remembered that the college, not the school, is the place for the complete study of a subject.

(To be continued).

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—We have read with great interest the article appearing in the Chem. News, vol lx., p. 184. Permit us to correct herewith some erroneous statements which it contains.

The quantities actually used at Wimbledon per 1000 gallons are about 6½ lbs. of lime and about 6½ ozs. of herring brine.

Blyth's experiments, to which you refer and which are in accord with those of Koch (see *Mittheilungen aus dem Kaiserlichen Gesundheitsamte-Berlin*), do not traverse Dr. Klein's results or our claim.

We do not claim any disinfecting power for amines, but for a new reagent evolved therefrom by the action of the lime.

When we characterised other sludges as a nuisance, we meant, of course, only *wet* sludges; we are not aware of any other process which claims, and can prove, for its *wet* sludge that it is inoffensive.

We shall be obliged by your inserting this in your next issue.—Yours &c.,

Hugo Wollheim.

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CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 12, September 16, 1889.

Evaporation-Heat of Carbonic Acid near the Critical Point.—E. Mathias.—A mathematical paper, not susceptible of useful abridgment.

Supplementary Thermic Data.—J. Ossipoff.—The author determines the hydration-heat of maleic anhydride and the neutralisation-heats of the maleic and fumaric acids.

Thermic Formation of the Salts of Phenylendiamines.—Leo Vignon.—The author gives thermochemical data yielded by the meta- and ortho-compounds.

Alcoholic Fermentation of Honey and the Preparation of Mead.—G. Gastine.—Solutions of honey do not readily undergo the alcoholic fermentation, even in the most favourable circumstances. The author overcomes this difficulty by adding to the honey the mineral salts necessary for the growth of the ferment, and a small quantity of bibasic ammonium phosphate and neutral tartrate. The solutions of honey should first be sterilised by boiling and closed with a plug of wadding.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xx., No. 2.

Molecular Combinations of Camphor.—P. Cazeneuve.—Already noticed.

Action of Borax upon the Polyatomic Alcohols and Phenols.—A. Lambert.—Borax may serve as a reagent for showing if a sugar possesses the primary function, and if a polyatomic phenol belongs to the ortho-series.

Rapid Determination of Saccharine Matter with a Decinormal Cupro-potassic Solution.—J. E. Politis.—The difficulty in determining sugars with Fehling's liquid is the detection of the end of the process. The author uses a decinormal Fehling's liquid in excess, and after reduction he determines the excess of copper by De Haen's method with potassium iodide and sodium thiosulphite.

Detection of Chicory in Coffee.—M. Baumert (*Journal de Pharm. de Lorraine*), Karz.—The author founds his process on the excess of chlorine in chicory, which is nine times greater than in coffee. He incinerated 25 grms. of genuine coffee, treated the ash with an alkali, and lixiviated it with water slightly acidified with nitric acid. The liquid required 7·5 c.c. of normal silver nitrate. The same quantity of chicory requires 70 c.c. of the solution (1 c.c. represents 1 milligrm. of chlorine).

MISCELLANEOUS.

The Utilisation of Cow's Milk.—As hitherto no experiment has been made as to the utilisation of cow's milk by adult persons the author made an investigation of this kind on a healthy powerful labourer. This man took for three days daily 3 litres of milk, which he consumed without repugnance and which occasioned him no inconvenience. The milk and the excreta were analysed. In spite of the large quantity of milk the body was not in equilibrium as regards nitrogen, since the milk contained only 39·84 grms. nitrogen, whilst 61·51 grms. were expelled in the excretions. The experiment proved that of all animal and most vegetable foods milk is least completely utilised in the body of the adult. Children utilise it better.—*Zeitschr. f. Biologie* and *Chemiker Zeitung*.

Action of Soaps and Fatty Acids in the Animal Body.—The author shows that on the injection of small doses (0·08 to 0·09 grm. per kilo. of body-weight) into the blood of rabbits, the beats of the heart, after a short transitory acceleration, became slower and feebler, whilst the consumption of oxygen and the excretion of carbon dioxide fell to from one-half to one-fourth of their value as previously ascertained. On stronger injections (0·14 grm.) the heart beat still more slowly, and finally came to a stand. Check experiments with volatile fatty acids showed that of them doses from five to seven times larger did not weaken the action of the heart. Further experiments on the action of the soda soaps upon dogs showed that these soaps had more paralysing effect upon the heart the more rapidly they were introduced into the circulation. — *Central-Blatt. Med. Wissenschaft* and *Chemiker Zeitung*.

The Principal Cause of the Attenuation of the Poison of Rabies.—According to the view of Pasteur dry air is the chief cause of the attenuation of the virus of rabies. M. Protopopoff has demonstrated that this virus may be preserved in a pure state if a piece of the spinal marrow of a rabbit which has died of rabies is placed in glycerin broth which has been sterilised in the steam apparatus of Chamberland. The poison of rabies very quickly loses its poison property even in glycerin broth if it is kept at a higher temperature. He has proved that the attenuation of the virus in the system of preserving the vaccine for rabies in glycerin broth is in direct relation to the temperature, and that the latter is the sole cause of the attenuation of the poison on Pasteur's principle.—*Central-Blatt f. Bacteriologie* and *Chemiker Zeitung*.

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See opinion *Electrical Review*, October 21.

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THE MANUFACTURE OF ALUMINIUM FROM CRYOLITE.*

By Professor P. PHILLIPS BEDSON, D.Sc.

At the last meeting of the British Association in this city the manufacture of aluminium formed the subject of a paper read before this Section by our President, Sir Lowthian Bell, in which an account was given of the method practised at the Washington Chemical Works, where the manufacture of aluminium had then been in operation for some three and a half years. Shortly afterwards this interesting manufacture ceased to be a local industry, but the present year has witnessed the return of this manufacture to the Tyneside, where it promises to make a home for itself. These facts in themselves would form a sufficient excuse for laying before the members of this Section an account of this industry, but inasmuch as the method of manufacture at present practised on the Tyne is one of an entirely novel character, an apology for a description of such a process is scarcely needed. For whilst the process described by Sir Lowthian Bell in the paper, already referred to, is the one due to H. St. Claire Deville, viz., that dependent on the decomposition of the double chloride of aluminium and sodium by metallic sodium, which is also used at the Oldbury Works, Birmingham, and recently described by Sir Henry E. Roscoe, the method described in this paper is dependent on the decomposition of the mineral cryolite, a double fluoride of sodium and aluminium, by metallic sodium. The credit of the successful application of this decomposition to the manufacture of aluminium on an industrial scale is due to Professor Netto. To the kindness and courtesy of Professor Netto I am indebted for the details of the methods employed, as also for the opportunity of witnessing their practical application at the works of the Alliance Aluminium Co., Limited, Wallsend.

The various processes which have been suggested for the manufacture of aluminium since the discovery of this metal; and which have, in any way, proved to be of practical value, may be summarised as follows:—

(1). *Electrical Methods.*

a. The electrolytic decomposition of halogen compounds of aluminium in a fused state.

b. The electrolytic decomposition of oxygen compounds of aluminium.

c. The electro-thermal decomposition of oxygen compounds of aluminium in presence of carbon.

(2). *Metallurgical Methods.*

By the decomposition of molten halogen compounds of aluminium by means of metals having a strong affinity for the halogen elements, such as sodium, potassium, or magnesium.

The only processes capable, in practice, of yielding a pure and unalloyed metallic aluminium are the metallurgical, of which there are two.

The older of these is Deville's method. This mode of producing aluminium necessitates first, the manufacture from a suitable natural aluminiferous material of hydrate of alumina. Secondly, the conversion of this hydrate of alumina into the double chloride of aluminium and sodium, $AlCl_3(NaCl)_3$, which conversion is effected by submitting a mixture of the hydrate of alumina, carbon, and common salt, heated at a high temperature in retorts to the action of chlorine, condensing, and collecting the double chloride produced in suitable vessels. The third series of operations is the decomposition of the double chloride so obtained by means of metallic sodium.

The second metallurgical method is that due to Professor Netto, in which the mineral cryolite, a compound similar in chemical constitution to the chloride of aluminium and sodium, from which it differs in containing the element fluorine, instead of chlorine, its composition being expressed by the formula $(NaF)_3AlF_3$, is substituted for the double chloride of aluminium and sodium, and which, after admixture with suitable fluxes, is decomposed by metallic sodium. Although it has been known since 1855 that cryolite can be decomposed by sodium so as to yield its aluminium in the form of the metal, an observation made by the late Dr. Percy and Heinrich Rose, still it is only within the last two years that these facts have remained anything more than a matter of purely scientific interest. Many attempts have been made to utilise this reaction in practice, but hitherto the difficulties associated with its application have proved too great.

Amongst these difficulties may be enumerated, first those arising from the high melting-point of cryolite itself. The temperature at which this mineral melts is such that when metallic sodium and cryolite are intimately mixed, and the mixture heated to the point needed in order that the sodium may act upon the cryolite, the greater portion of the sodium is volatilised before it has performed its work. The second main hindrance to the use of cryolite arises from the fact that this mineral is always associated with quartz or other siliceous minerals, which, by reason of their physical properties, it is impossible to separate by any mechanical means. As these compounds also are decomposed with the fluoride of aluminium by the sodium, and in such a way as to yield silicon, the latter unites with the aluminium produced, in fact is concentrated in the metal obtained, and materially affects its physical properties and consequent utility in the arts. These difficulties have been succesfully overcome, the first by fusing the cryolite before introducing into it the metallic sodium, which is effected by means of a special appliance, the sodium being submerged in the molten liquid; thus loss by volatilisation and its combustion is prevented.

Manufacture of Aluminium.

In practice the decomposition of cryolite by metallic sodium represented by the equation—

$$3Na+(NaF)_3AlF_3=6NaF+Al$$

is effected in two ways. On the large scale, a charge consisting of 200 lbs. of cryolite, mixed with 200 lbs. of salt, is melted in a reverberatory furnace. The fusion of this mixture requires about an hour and a half for its completion; the molten charge is then run into an iron converter which has been previously warmed. A block of sodium weighing about 5 lbs. is next thrown into the molten mass and immediately submerged by means of a "dipper" worked by two men. The "dipper" consists of a long iron bar, in the middle of which, and at right angles to it, is a second iron rod, to the free end of which is attached a circular piece of sheet iron, slighly concave, and studded throughout with holes. This circular piece of iron fits into the converter, and is worked up and down by a man stationed at each end of the long bar. Immediately on the sodium being brought into contact with the molten cryolite and salt, it is covered by the dipper and slowly depressed through the mass. This operation is repeated until the requisite quantity of sodium has been used, which for such a charge would be some 40 lbs. The introduction of the sodium is attended by a violent reaction, and at the commencement of the "dipping" the temperature rises and a considerable ebullition takes place, accompanied by production of flame and dense white fumes, consisting chiefly of sodium fluoride.

* Read before the British Association, Section B, Newcastle Meeting.

the dipping proceeds the mass grows darker and the reaction attending the introduction of the sodium less violent. When the required quantity has been introduced the bulk of the slag is poured oft by tilting the converter, which is suspended on trunnions, into a large iron pot, and the last portion, containing the aluminium, is poured into a small iron vessel, in which, on cooling, the aluminium is found collected together in a mass. The separation of the greater bulk of the slags in this way is essential to the successful extraction of the aluminium, since, if the whole mass were allowed to cool, the separated aluminium would gradually dissolve up again in the slags.

A notable feature is the short time required to effect this decomposition of the cryolite by sodium, which does not allow of any loss by volatilisation of the sodium, nor is there any opportunity for a loss by its combustion, since it is always covered by the molten liquid, and thus protected from the action of the air. By this comparatively simple method of manipulation, what might otherwise be a very dangerous operation is effected without any great risk of injury to the workpeople, who are also protected against accident by special gloves and masks.

Working in this manner, and with a pure cryolite, the aluminium obtained would be practically pure, and from the amount of cryolite mentioned above the weight of aluminium produced would be about 10 lbs., requiring about 40 lbs. of sodium for its production. The slags produced contain about 40 per cent of sodium fluoride, 43 per cent of sodium chloride, 15 per cent of cryolite, and some alumina, together with about 0·75 per cent of metallic aluminium in a fine state of division scattered throughout the mass.

The mention of the finely-divided aluminium brings to mind one of the difficulties associated with the manufacture of this metal, which, by reason of its lightness, does not sink through the slag produced, as is the case in the production of other metals.

The second difficulty attending the use of cryolite as a source of aluminium is due to the impurities contained in native cryolite, impurities varying in amount from 1 to 3 per cent. The influence of these impurities is overcome by making use of the fact that the chief of these, viz., the compounds of iron and silicon, are reduced by sodium before the fluoride of aluminium is attacked. To this end the molten mixture of cryolite and flux is dipped with one-third of the sodium required for its decomposition; in this manner the iron and silicon are precipitated with some aluminium, and the liquid poured off from this into another hot converter; this again is treated with the remainder of the sodium needed. With an ordinary cryolite, by this method of "double dipping" a metal containing from 98 to 99 per cent of aluminium is easily obtained. For special classes of aluminium of the very best manufacture working in crucibles is adopted, since, in this way, a better control of the liquid mass of cryolite and flux is obtained, as the crucible stands in the furnace during the whole operation of "dipping." In such cases the practice of "double dipping" is always resorted to. The crucibles employed are made of fire-clay and manufactured by Messrs. Morgan, of London; these are heated in furnaces built in the floor, similar to those employed by steel melters; the fuel used is coke. The introduction of the sodium into the molten mass in the crucibles is effected by fastening a block of sodium to an iron rod, and covering it with a circular piece of metal provided with holes, and also a slit in which the rod fits. The circular piece of metal is attached to a rod of iron, which serves to keep the cover over the sodium. By the aid of these appliances the sodium can be introduced into the molten liquid under conditions similar to those in which it is used in the working on the large scale.

I am led to understand that the Alliance Aluminium Co., which uses Prof. Netto's method, classify the aluminium produced in the above-mentioned manner as follows:—

Class AA, produced in crucible and by "double dipping," 98·5—99 per cent aluminium.

Class A, produced in converter and by "double dipping," 97—98·5 per cent of aluminium.

Class B, produced in converter and by single dipping, 95—97 per cent of aluminium.

Class C, produced in converter and by "double dipping," being the first product of the "double dipping," 90—95 per cent aluminium.

Another point, and one of considerable interest in connection with the production of aluminium from cryolite is the composition and regeneration of the slags. These slags contain some 40 per cent of sodium fluoride, and also some $\frac{3}{4}$ per cent of metallic aluminium. Prof. Netto informs me that this metallic aluminium has been recovered from these slags by melting the slag with metallic copper, and producing in this way an aluminium bronze. From the slags, after treatment with metallic copper, cryolite can be reproduced by heating the slags together with aluminium sulphate, in suitable proportions, and extracting the sodium sulphate found by a subsequent treatment with water. The reaction upon which this regeneration depends is expressed as follows:—

$$12NaF + Al_2(SO_4)_3 = 3Na_2SO_4 + 2Na_3AlF_6.$$

This simple method of utilising the slags formed for the production of cryolite—a cryolite which in many ways is purer than native—places the manufacture of aluminium from cryolite on a better footing than its production from the double chloride of sodium and aluminium.

The following are the amounts of the various materials required for the production of one part by weight of aluminium:—

12	parts	by weight of	cryolite.
12	,,	,,	common salt.
20	,,	,,	coal.
3	,,	,,	sodium.

At the same time there are produced 20 parts by weight of slags containing 40 per cent of sodium fluoride, 15 per cent of unreduced cryolite, 43 per cent of salt, a small proportion of alumina, and some $\frac{3}{4}$ per cent of finely-divided aluminium.

From the above it is evident that the production of aluminium by this method is largely dependent upon the cheapening of the manufacture of sodium, of which metal from 3—4 parts are required for the manufacture of 1 part of aluminium, the theoretical proportion being 2·5 of sodium to 1 of aluminium. Consequently, in recent years, many efforts have been made to reduce the cost of sodium production and improve the existing methods. Of all these attempts the most successful have been those in which caustic soda has been substituted for the carbonate of soda. The use of caustic soda in the manufacture of sodium is dependent on the observation first made by Curaudau, shortly after the discovery of metallic sodium by Davy, that caustic soda is decomposed when heated with carbon, and metallic sodium produced. The decomposition may be represented by the following equation—

$$2NaOH + C_2 = Na_2 + 2CO + H_2.$$

The main difficulties attending the use of caustic soda in this way are those arising from its easy deliquescence, and secondly, from the ease with which it passes, when fused, into a thin mobile liquid, which prevents the permanent establishment of an intimate admixture of the reducing agent. Inasmuch as the decomposition of the caustic soda by carbon takes place at a lower temperature than that of the carbonate, the cheapening of the production of sodium in this way has been found to be possible, despite the difference in price between the carbonate and caustic. The reaction, however, is not in reality as simple as the above equation would lead one to imagine, for a portion of the caustic soda is converted into carbonate of soda, which would require a higher tempera-

ture for its decomposition. The formula of carbonate of soda may be represented as follows:—

$$4NaOH + C_2 = Na_2CO_3 + Na_2 + 2H_2 + CO.$$

Castner has overcome one of the chief difficulties attending the use of caustic soda by weighting the carbon by previous fusion with metallic iron, but in heating this mixture the carbonate of soda produced, as represented by the equation above, serves to dilute the caustic soda, and necessitates the use of retorts or crucibles made of steel or wrought iron, in which the materials can be raised to a temperature sufficiently high to decompose the carbonate of soda and the caustic. Professor Netto has surmounted these difficulties by effecting the removal of the carbonate of soda, as it is produced, from the zone of decomposition, and he has, consequently, been enabled to make full use of the comparatively low temperature at which caustic soda is decomposed by carbon, and to utilise cast-iron retorts for this purpose. To this end fused caustic soda is allowed to flow in a carefully regulated stream over a mass of heated charcoal contained in a retort, the gaseous products pass through an opening in the top of the retort, and the sodium condenses and is collected in an iron pan; the undecomposed caustic soda and the carbonate of soda collect at the bottom of the retort, and are drawn off from time to time.

This method will perhaps be made more intelligible by a description of the plant employed. The retorts made of cast-iron are pear-shaped, and about three feet in height; at the bottom is a tubulus closed by a plug, and serving for the withdrawal of the slags. Fitting on to the top of the retort is a lid with three openings; one serves to convey the gases and vapours produced to the condensing apparatus; the second opening is used for the introduction of the charge of the reducing carbon; and the third, which is surrounded by a cup, is closed by a screw-valve, by which the flow of fused caustic soda can be regulated. The retort is supported on brick-work, and is surrounded by a circular furnace, in which coke is used as fuel. The heated gases are led away at the top of the retort, at a point below the lid, into a chamber in which is built an iron box, in which the caustic soda is melted by the heated gases from the furnace. The iron box is provided below with an aperture opening into a channel along which the liquid caustic soda is conducted to the cup on the lid of the retort. The opening in the iron box is also closed by a screw-valve, which further serves to regulate the supply of liquid caustic soda to the retort. Fitting on to the top of this iron box is another closed by a lid, and provided at one side with a slide, which can completely divide the upper box from the lower one, and thus prevent the solid caustic soda from falling suddenly into the fused mass below. The upper box having been filled with solid caustic soda it is then closed by the lid, and the slide gradually withdrawn to allow the solid caustic soda to fall into the vessel below, in which it is melted.

In this manner a portion of the caustic soda is decomposed and metallic sodium produced; the portion partially converted into carbonate collects at the bottom of the retort, and is drawn off from time to time, forming what is styled a soda slag. The soda slags can either be re-causticised or sold to paper manufacturers and others, and, in fact, find a ready sale.

Every twelve hours the process of sodium production is interrupted for a short time for the purpose of re-charging the retort with charcoal. Such a retort will yield 42 kilogims. of sodium in a day, and will produce 750 kilogrms. of the metal before it is so acted upon as to necessitate a renewal.

The following are the amounts of the several materials required for the production of one part by weight of sodium:—

10	parts	of caustic soda
1·2	,,	cast-iron for the retorts
12	,,	coke
1·5	,,	charcoal for reduction.

At the same time nine parts of soda slags are produced, consisting chiefly of carbonate of soda and some caustic soda, containing about 60 per cent Na_2O.

In conclusion, I must express my great indebtedness to Professor Netto for the kind manner in which he has assisted me, in furnishing the information with which it has been possible for me to give an account of the latest Tyne-side industry. Further, I am indebted to Professor Netto and the Alliance Aluminium Company, of Wallsend, for the specimens and photographs illustrating the manufacture of sodium and of aluminium from cryolite.

ANALYTICAL STUDIES ON PHOSPHODODEKAMOLYBDIC ACID, THE CONDITIONS OF ITS FORMATION, AND ITS SEPARATION AS AN AMMONIUM SALT.

By Dr. FRANZ HUNDESHAGEN.

(Continued from p. 189).

Mineral acids considerably attack the ready-formed precipitate, even in presence of ammonia, and especially on the application of heat. The colourless acid solutions separate out the dissociated phosphomolybdate, neutralising the excess of acid. Nitric acid seems to act most slightly, hydrochloric acid more strongly, and sulphuric acid most of all.

The following experiment may prove how intense is the decomposition of the ready-formed precipitate by nitric acid, even in presence of ammonium nitrate:—

In a neutral solution of 0·010 grm. P_2O_5, 0·243 grm. MoO_3, and about 10 grms. NO_3NH_4, the phosphomolybdate was thrown down by a slight excess of nitric acid. A few drops of molybdate solution produced in the solution (the volume of which was about 50 c.c.) no trace of a precipitate; but after about 1000 mols. NO_3H (20 c.c. of the nitric acid used in an experiment already described) had been further added, and the whole had been heated nearly to a boil, there appeared again a precipitation with molybdic acid, until altogether 0·051 MoO_3 had been further added. The separation of the P_2O_5 required now about 21 per cent MoO_3 more than before, showing that in such a short time about one-fifth part of the precipitate had been decomposed by the acid. If the heating had been prolonged probably half the precipitate would have been destroyed.

Organic polybasic acids, oxalic or tartaric acid, and their salts decompose the precipitate in heat very readily. Their presence, as already intimated, hinders the re-union of the phosphoric and the molybdic acid under all circumstances.

The action of reducing agents did not come within the scope of the author's investigations.

Of all the substances above named the most suitable for washing the ammonium phosphomolybdate are faintly acidulated solutions of ammonium nitrate or chloride, both cold and warm, of which about five per cent in the washing water is sufficient; then follows acidulated solution of ammonium sulphate (five to ten per cent), as also dilute nitric or hydrochloric acid (one to two per cent), but these acids must not be left long in contact with the precipitate. For neutral washing, cold solutions (about five per cent) of neutral ammonium nitrate or chloride, or for rapid washing, ice-cold water. Water at common temperatures must be avoided, as even with the greatest care traces of the precipitate can scarcely be prevented from passing through the filter or becoming dissolved.

Such a small loss on washing with water is the cause why Hehner divides the weight of the residue by 28·5 in order to find the correct weight of P_2O_5.

7. *The Titration of Phosphoric Acid with Molybdic Acid, and that of Molybdic Acid with a Solution of Phosphoric Acid.*

In order that the quantity of P_2O_5 present may be correctly inferred from the quantity of MoO_3 consumed in precipitating the phosphoric acid, the quantity of nitric acid which co-operated in the formation of the ammonium phosphomolybdate must be known at least approximately.

This knowledge is acquired and the object is attained, so that at any moment a degree of acidity favourable to the formation of phosphomolybdic acid is present, by making the solution to be titrated neutral or very slightly acid, and to the solution of molybdic acid there is added at the outset not more and not less than the quantity of nitric acid most favourable for the formation of the phosphomolybdate in a neutral solution and for its rapid separation, *i.e.*, to 1 mol. MoO_3 about 3—4 mols. NO_3H, corresponding to 36—48 mols. to 1 mol. of the phosphomolybdate to be precipitated. After the formation of the precipitate the solution would contain only about 10—22 mols. of free nitric acid. It will be remembered that in a solution with this proportion of acid the influence of dissociation is imperceptible, and in such a one the mol. of P_2O_5 is thrown down quantitatively by 24 mols. MoO_3.

For the titration of small quantities of phosphoric acid the author uses with success:—

Ten grms. pure molybdic acid (or 12·262 grms. pure crystalline hexammonium heptamolybdate) are dissolved in an excess of dilute ammonia, the liquid is mixed with about 15 grms. NO_3H (*e.g.*, 39 c.c. nitric acid of sp. gr. 1·20) and diluted to 1 litre. It contains thus per mol. of neutral molybdate 3·43 mols. NO_3H, or per mol. of free MoO_3 1·43 mols. of free NO_3H, which suffice along with the ammonium phosphomolybdate precipitated in a neutral solution to leave an excess of about 15 mols. NO_3H (supposing that sulphates are absent).*

Of this solution there were consumed for the precipita- of 0·010 grm. P_2O_5, independent of the proportion of phosphoric acid in the liquid to be titrated (it contained about ten per cent of ammonium nitrate), from 24·3 to 24·5 c.c., that is the quantity of phosphoric acid theoretically required.

In titration the author proceeds as follows:—The neutral or slightly acid solution of phosphate, which does not need to contain in 100 c.c. more than 0·025 grm. P_2O_5, and which should not be more concentrated, is mixed with so much ammonium nitrate that in 100 c.c. it may contain 10—15 grms. NO_3NH_4, and is heated nearly to a boil. Small quantities of the molybdic solution—towards the end only drops—are run in until no further precipitate of ammonium phosphomolybdate appears. The presence or the absence of renewed precipitation is detected accurately and conveniently, and without filtering portions, as follows:—

Care must be taken by a suitable position of the Bunsen (or other burner) that the ascending current of the heated liquid is not in the front, but in that part of the vessel which is turned away from the observer, so that in those strata of the liquid which are nearest to the observer there is a slow downward movement which here effects a very gradual intermixture of the molybdic acid solution with the rest of the liquid. There is then placed close behind the vessel a piece of blue cobalt glass, so that its upper edge rises a few c.m. higher than the level of the liquid. If viewed against this glass the finest particles, the slightest traces of an incipient precipitate, are clearly apparent.

The molybdic solution is then let flow in along the front side of the vessel so that it may float upon the solution, which is specifically heavier. In the zone where the liquids mix there appears at once a dense pale yellow cloud, from which the precipitate, as it condenses, slowly *snows down*. The observer mixes, and whilst the precipitate subsides he removes the yellow stripes and coatings on the front side of the beaker, which would interfere with the observation of the phenomena, using a glass rod, the end of which is covered with a ring-formed piece of caoutchouc tubing. When the liquid has become sufficiently clear (which at first takes a considerable time, but becomes more rapid towards the end of the process) a little more molybdic solution is let flow upon the surface; after waiting a few seconds, until the precipitate has formed, the liquid is stirred and the process is continued in the same manner until the last drops no longer produce a cloudy zone. When, after adding 2 or 3 drops of the molybdic solution, there does not, in the course of half a minute, appear a faint stripe at that part of the side of the beaker where the drops entered the surface of the liquid, the precipitation may be regarded as complete. So long as this stripe is still visible (which is best seen along the upper edge of the meniscus if viewed from above at an angle of 45°) traces of phosphoric acid still remain in solution. This last character is especially important for the titration of small quantities of phosphoric acid.

The following examples show the accuracy which may be reached if all the precautions are observed:—

1. 0·00050 grm. P_2O_5 required for precipitation 1·260 c.c. MoO_3 solution. 0·0126 MoO_3 = 0·000518 P_2O_5.

2. 0·00025 grm. P_2O_5 required 0·598 c.c. molybdic solution. 0·00598 molybdic solution = 0·000246 P_2O_5.

3. 0·00040 grm. P_2O_5 required 0·972 c.c. molybdic solution. 0·00972 = 0·00040 P_2O_5.

The above mentioned molybdic solution keeps unchanged for months, even if exposed to frequent changes of temperature; less concentrated solutions deposit in time small quantities of molybdic acid; hence if it is desired to work with solutions containing a larger proportion of molybdic acid, there must be prepared a neutral titrated solution of molybdate and a titrated nitric acid, both being kept apart, and in the determination there must be used two burettes, or a kind of double burette, one tube of which contains the molybdic solution and the other the acid, from which each fluid is let flow alternately in proper proportions.

The method may be inverted and used successfully for the titration of molybdic acid by means of a solution of known value. In a solution of the right acidity 24 mols. MoO_3 are exactly precipitated by 1 mol. P_2O_5, whether the nitric acid is originally contained in the molybdic solution or it is introduced along with the phosphatic solution.

For practical purposes a neutral or slightly acid solution of molybdic acid is mixed with about 10 per cent of ammonium nitrate and titrated hot with a solution of sodium hydrophosphate, which contains, per mol. of P_2O_5, about 80 mols. NO_3H.

As it will be seen from the above, in titrating by the methods described, appreciable quantities of sulphates or other salts of polybasic acids would interfere, as also salts of monobasic organic acids. Polybasic organic acids and reducing agents must not be present. Small quantities of silica do not interfere. If appreciable quantities of salts of polybasic inorganic acids, such as sulphates, are present, the following expedient may be adopted:—

The faintly acid liquid to be titrated is first mixed with a known volume of the standard solution—say $\frac{1}{3}$ to $\frac{1}{2}$ of the total quantity required for precipitation—it is cautiously acidified with dilute nitric acid, until there is formed a permanent precipitate of ammonium phosphomolybdate and no longer increases, and the titration is then completed in the manner described above.

* Pure molybdic acid, free from phosphoric acid, can be quickly obtained in large quantities in a form readily soluble in ammonia by passing a strong current of air or steam through a boiling hot concentrated solution of ammonium molybdate. Ammonia is expelled from the solution, and a crystalline, snow-white, sparingly soluble molybdate is separated. By absorbing the moisture from the precipitate, washing in alcoholic water, repeated evaporation in case of need, solution in a little dilute ammonia, filtration, precipitation with alcohol, absorption of moisture, and oxidising ignition, a molybdic acid is obtained in the form of a dense white powder when cold.

In solutions rich in sulphate the phosphoric acid must be separated out in another manner and then re-dissolved in nitric acid for titration.

(To be continued).

WATER ANALYSIS.*

Having during the past two years given this matter our careful consideration, we beg herewith to submit the following report.

In order to ascertain the general feeling of chemists in this country on the subject, we have circulated the following series of questions amongst the leading water-analysts, upon whose co-operation the adoption of any uniform scheme must necessarily depend.

1. What is the system of recording the results of Water Analysis which you adopt?
   (*a*) For the Mineral matters.
   (*b*) For the Organic matters.
   (*c*) For the Gaseous matters.
2. Have you any objections, and if so what are they, to the use of a Decimal system—such as parts per million, per 100,000, per 10,000, or per 1000?
3. In recording the results of complete Analysis of the Mineral matters present in water, is it your custom to state the proportion of each individual Base and Acid as actually determined, or to combine the Bases and Acids so as to form salts?
4. Should it be your custom to combine the Bases and Acids, explain the principles by which you are guided in so combining them, and state what, in your opinion, are the advantages attaching to such combination.
5. If your present method of recording results is more or less influenced by special circumstances, such as the custom of professional Chemists generally, what other method of recording results would you yourself *select* as the most rational and the most convenient for universal adoption?
6. Would you support the adoption of the following method, recommended by the American Committee, of stating the constituents of a Mineral Water?—

"That the parts per thousand of each basic element, K, Na, Li, Ca, Mg, Fe" (Fe_2), &c., be given, and of each acidic element, such as Cl, I, S, &c., that is combined directly with a basic element, or that may reasonably be supposed to be so combined, the rest of the acidic elements to be given in connection with all the oxygen of their salts, as usually written in our present empirical formulæ, as SO_4, CO_3, PO_4, &c."

From the answers we have received to the above questions, as well as from our own personal experience, we gather that there would be no reluctance on the part of British Chemists to adopt a uniform and rational scheme, but for the great difficulty of rendering such a method of statement popularly understood. Thus the majority of analysts employ the "*grain-gallon*" system of statement, as being the one most intelligible to their clients, and this system undoubtedly possesses certain advantages in the case of analyses for technical purposes, in which the analytical figures have to be applied to large volumes of water which in this country are almost invariably measured in gallons.

We find, however, a general readiness on the part of most analysts to adopt a uniform and prescribed system only to be departed from in special cases, and we are of opinion that it would be impossible to secure more than such a qualified consent to any one system.

Although there is but little possibility of directly influencing the custom of professional chemists in their private practice, we are of opinion that it is of great importance to urge upon water-analysts the desirability of adopting some uniform system in the case of such analyses as are communicated to scientific societies or other learned bodies, and which are therefore calculated to have a circulation in countries where the imperial gallon is not recognised, and if such uniformity could be secured there is but little doubt that the system would before long establish itself even in the case of analyses of a non-public character.

As regards the method of statement which would be most suitable for general use in such published analyses, we are of opinion

(1). That it should be on the decimal system, preferably *parts per million* (m.grms. per litre) or *parts per* 100,000, as *parts per* 1000 (grms. per litre) would too frequently give rise to fractional results. The special advantages attaching to "parts per 100,000" are that the figures or mineral waters are not inconveniently large, nor those or potable waters inconveniently small, whilst their conversion into grains per gallon is a very simple operation.

We cannot agree with the American Committee that different scales should be adopted for mineral and potable waters respectively, for such a dual system must, in our opinion, inevitably lead to confusion.

(2). We attribute the greatest importance above all to the clear statement, in every case, of the actual determinations made, and that all results derived by calculation should be sharply distinguished from those obtained by direct determination.

Thus we view with particular disapprobation the statement of the mineral ingredients combined as *salts*, unless accompanied by a clear account of the analytical data upon which this statement is founded.

(3). As regards the statement of the mineral ingredients, we have considered the method suggested by the American Committee, and which consists in recording the proportion of each metallic element (K, Na, Li, Ca, Mg, Fe", Fe_2, &c.), as well as that of each electro-negative element (F, Cl, Br, I, S, &c.) contained in binary compounds, whilst in the case of oxy-compounds the electro-negative element is given as combined with the the whole of the oxygen (SO_4, PO_4, NO_3, CO_3, &c.), and we are of opinion that this arrangement is decidedly the most convenient for all purposes of calculation, although the absence of any recognised names for these acid-groups, as well as the prevailing custom of estimating the metallic elements in the condition of bases (K_2O, Na_2O, CaO, &c.) are undoubted objections to this system.

(4). That the amount of dissolved gases (O, N, CO_2, SH_2, &c.) may be most conveniently expressed either in cubic centimetres per litre or in volumes of gas per 100 volumes of water, the latter being the more general practice in this country.

The system of statement which we wish to recommend will be most readily understood from the following form for a complete analysis:—

Results of Analysis Expressed in Parts per 100,000.

Potable Water:—

Total solid matters	(*a*)	In suspension ..
	(*b*)	In solution ..
Organic carbon		
Organic nitrogen		
Oxygen consumed, as indicated by decolouration of permanganate		
Ammonia expelled on boiling with sodium carbonate		
Ammonia expelled on boiling with alkaline permanganate		
Nitrogen as nitrates and nitrites		
Chlorine		
Hardness	Temporary	
	Permanent	
	Total	

* Report of the Committee, consisting of Professors Dewar, E. Frankland, Percy F. Frankland (Secretary), and Odling, and Mr. Crookes, appointed to confer with the Committee of the American Association for the Advancement of Science with a view of forming a uniform system of recording the results of Water Analysis. Read before the British Association, Section B, Newcastle Meeting.

Mineral Water :—

Carbonate of lime ($CaCO_3$)	
Carbonate of magnesia ($MgCO_3$)	
Carbonate of soda (Na_2CO_3) (calculated from residual alkalinity after boiling and filtering off precipitated $CaCO_3$ and $MgCO_3$)	
Total calcium (Ca)	
Total magnesium (Mg)	
Total potassium (K)	
Total sodium (Na)	
Iron (ferrous) (Fe")	
Iron (ferric) (Fe_2)	
Sulphuric radical (SO_4)	
Nitric radical (NO_3)	
Nitrous radical (NO_2)	
Phosphoric radical (PO_4)	
Silicic radical (SiO_3)	
Chlorine (Cl)	
Bromine (Br)	
Iodine (I)	
Sulphur as sulphide (S)	

Dissolved Gases.

Cubic Centimetres of Gas at 0° C., and 760 Millimetres in 1 Litre of Water.

Carbonic anhydride (CO_2)	
Oxygen (O)	
Nitrogen (N)	
Sulphuretted hydrogen (H_2S)	

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

(Continued from p. 196).

WITH the object of presenting in an available form information as to the position occupied by chemistry in Board and other Public Elementary Schools, which are controlled either by the Education Department, Whitehall, or the Science and Art Department, South Kensington, the Committee now present a report on the subject which has been prepared by Professor Smithells. A consideration of this statement will show that, as in the higher grade public schools, with which the Report of the Committee last year was chiefly concerned, the condition of the teaching in public elementary schools is far from satisfactory. As a rule chemistry is not taught on the proper lines. The pupils frequently receive the same kind of instruction in chemistry as they would at a later stage if they were preparing for a professional or technical career; consequently the subject has failed to provide that mental education which it should be the main object of elementary teaching to develop. It appears, too, that in many of these schools physical science has not hitherto been regarded as a necessary part of the educational scheme. It is essential that this state of affairs should be altered, and that physical science should occupy a more favourable position in the Education Code, and that its teaching should be more thoroughly controlled.

It is to be hoped, also, that the Education Department, as well as the Science and Art Department, South Kensington, will take steps to arrange a more efficient mode of inspecting science teaching than that at present in vogue, which can only be regarded as satisfactory from a purely statistical standpoint. Under the present system little or no control can be exercised over the science teaching, since the Whitehall Inspectors are, as a rule, not qualified to form an opinion as to its value. There would seem to be no difficulty in obtaining the services of properly qualified persons to act as additional inspectors for the purpose of reporting on the character of the science teaching. It is probable that many of the professors and lecturers in University Colleges, and other educational institutions, might be willing to take part in such inspection, and it would thus become possible to maintain a high standard of excellence in the teaching.

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe. Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

*The Teaching of Chemistry in Public Elementary Schools.**

Drawn up by Professor SMITHELLS.

In view of the rapid increase in the teaching of chemistry in connection with public elementary schools likely to take place, chiefly on account of the establishment of the so-called "Higher Grade Board Schools," and in view of the strenuous attempt that is being made to extend the teaching of science subjects by a separate Act dealing with technical instruction, it seemed of importance to prepare a short statement indicating the position occupied by chemistry in our state-aided elementary schools. Since the chemical teaching in such schools is practically dominated by the syllabus of the Education Code and of the Science and Art Department, any improvements or suggestions the central authorities at Whitehall or South Kensington could be induced to accept would at once take effect throughout public elementary schools dealing with four and a half millions of children, or between one-sixth and one-seventh of the total population.

The following statement deals with the conditions under which chemistry is taught in Voluntary and Board Schools, and with the extent of such teaching, in England and Wales only. Notes are added with reference to chemistry teaching under the Scotch Edacation Department, and to other matters relating to the main question.

The Education Code.—The subjects of instruction in the Education Code are divided into three classes :—

1. ELEMENTARY OR COMPULSORY SUBJECTS.—Reading, Writing, and Arithmetic (and Needlework for girls).
2. CLASS OR OPTIONAL SUBJECTS.—English, Geography, Elementary Science, History, Singing, or other graduated subject approved by the Inspector.
3. SPECIFIC SUBJECTS.—Algebra, Euclid and Mensuration, Mechanics, Chemistry, Physics, Animal Physiology, Botany, Principles of Agriculture, Latin, French, Domestic Economy, and other subjects approved by the Inspector.

All schools must take the elementary subjects in all the standards.

Not more than two class subjects may be taken, one being English. (In the case of girls the second class subject must be needlework unless taken under the head of elementary subjects).

The specific subjects are only to be taken in the upper classes of a school, viz., in Standards V., VI., and VII.

There is in the Code as it stands the possibility of an excellent course of instruction in elementary chemistry. It would really begin in the infant school with enlightened object lessons and kindergarten work, then in the elementary school proper it could be continued in the first four standards as the class subject "elementary science," lastly, in the V., VI., and VII. Standards as the specific subject chemistry.

The teaching in the infant schools is not circumscribed by detailed schedules or individual examination, and is admittedly the most satisfactory part of our educational system.

The schedule for elementary science as a class subject is as follows :—

* *I.e.*, in Voluntary and Board Schools receiving grants from the Education Department under the Education Acts.

Standard I.	Standard II.	Standard III
III. Elementary Science. A progressive course of simple lessons on some of the following topics, adapted to cultivate habits of exact observation, statement, and reasoning.	Common objects, such as familiar animals, plants, and substances employed in ordinary life.	

Standard IV.	Standard V.	Standard VI.	Standard VII.
A more advanced knowledge of special groups of common objects, such as— (*a*) Animals or plants, with particular reference to agriculture. (*b*) Substances employed in arts and manufactures. (*c*) The simpler kinds of physical and mechanical appliances, *e.g.*, the thermometer, barometer, lever, pulley, wheel and axle, spirit level.	(*a*) Animal or plant life. (*b*) The chemical and physical principles involved in one of the chief industries of England, among which agriculture may be reckoned. (*c*) The physical and mechanical principles involved in the construction of the commoner instruments, and of the simpler forms of industrial machinery.	The preceding in fuller detail.	The preceding in fuller detail.

Chemistry as a specific subject taken by boys in the V., VI., and VII. Standards is divided into three "stages" as follows, each stage representing one school-year's work:—

Stage I.	Stage II.	Stage III.
Elementary and compound matter. Illustrations of combination and decomposition in such bodies as hydrochloric acid, water, oxide of mercury, and rust of iron.	Preparation and properties of the common gases, such as oxygen, hydrogen, nitrogen, and chlorine. The chemical character and constituents of pure air and pure water, and the nature of the impurities sometimes found in both. Effects of plants and animals on air.	The properties of carbon and its chief inorganic compounds. Differences between metallic and non-metallic bodies. Combination by weight and volume. The use of symbols & chemical formulæ.

Any *further teaching* of chemistry than the above would not earn Government grants from the Education Department, but might be provided by school managers in extra classes or in a so-called Higher Grade School by money from the school funds or the rates (according as it were a Voluntary or Board School) and by means of grants obtained from the South Kensington Science and Art Department under conditions to be subsequently explained.

Inspection and Grants.—The teaching of the science in all stages would be subject to the inspection of one of H.M. Inspectors of Schools, on whose annual report the Government grant would be awarded. The examination, conducted once a year, in the elementary science is oral, and may be conducted as the Inspector likes. If the class is reported "fair" a grant of 1s. per head is allowed, if "good" 2s., and besides this the quality of work done in the class subject is considered in awarding the "merit grant," *i.e.*, a grant awarded to the school on the general merits of the organisation, teaching, and discipline, 1s., 2s., or 3s., according as it is "fair," "good," or "excellent."

In 1887-8, 25,000 out of 4,500,000, *i.e.*, 1 in 180, children in schools took this subject.

The teaching of chemistry as a specific subject is also under the control of H.M. Inspectors, who award a grant of 4s. on each pupil who passes at the annual written examination. The performance in specific subjects also counts in awarding the merit grant.

Teachers and Apparatus.—The teachers in the earlier standards (including elementary science) are the usual school teachers, and have not necessarily any qualification of a scientific kind.

The inspectors have instructions to ascertain that teachers of *specific* subjects have received training in a training college or have passed some public examination. The Department recommends the "peripatetic" system of science teaching by a "demonstrator," in which either the demonstrator visits the schools in rotation, or the pupils from the different schools attend a central laboratory for science instruction. This system has been adopted with success in several large towns, including London, Liverpool, Manchester, Birmingham, and Leeds.

There is no stipulation in the Code for apparatus or experimental illustration, this being a matter for the school managers, subject to the criticism of the inspectors.

Statistics.—The following are statistics as to the teaching of chemistry in elementary schools as a specific subject under the Whitehall Code for the year 1887-8:—

	Total No. examined.	Passed.	Per-centage.	1st stage.	2nd stage.	3rd stage.
Voluntary schools	453	327	72·2	181	127	19
Board ,,	1035	750	72·5	409	295	46
Total..	1488	1077	—	590	422	65

	Average number of scholars in attendance in all subjects.	Proportion taking chemistry (specific).
Voluntary schools ..	2,216,854	about 1 in 5000
Board schools	1,327,710	,, ,, 1280

The proportion taking chemistry in Board schools is thus about four times that in Voluntary schools.

Chemistry as a Science Subject.—The preceding statements apply only to teaching under the Whitehall Education Department. The greater part of the chemistry teaching is carried out under the Science and Art Department, South Kensington. This is done in virtue of a regulation of that Department, whereby pupils in elementary schools receiving aid from the Whitehall Education Department may be "registered" in a science subject provided that they have passed Standard VI. of the Code and are taught by a duly qualified teacher. Such teacher must have obtained a first class in the advanced stage of the May examinations of the Science and Art Department, or have obtained some qualification deemed equivalent by the Department.

Pupils who have passed Standard VI. may thus form a class under the Science and Art Department, and present themselves at the usual May examinations in chemistry.

For every pass in the elementary or advanced stage a payment of £2 for a first class and £1 for a second class is made, subject to a deduction of 4s. if the same pupils have within the previous six months been examined and have obtained grants through the Whitehall Department for chemistry as a specific subject.

For honours £4 and £2 for a first and second class, respectively, are granted.

In practical chemistry the following grants are made:—

£2 and £1 for first and second class elementary respectively
£3 „ £2 „ „ advanced „
£4 „ £3 „ „ honours „

The conditions are :—

(*a*). That the teacher is qualified as above.
(*b*). That he has given at least 28 lessons during the session.
(*c*). That each candidate has received 20 lessons.
(*d*). That the candidate does not present himself in more than two subjects.

Stringent conditions are also made as to laboratory accommodation and the provision of apparatus, and grants are made for these purposes.

The teaching is under the inspection of the South Kensington inspectors, who are only four in number. They are assisted by "acting inspectors," consisting of officers of the Royal Engineers, who may inspect classes in the neighbourhood where they are for the time stationed. Such inspection is, however, as a rule, merely "statistical" as to apparatus and laboratory fittings.

The syllabus of the examinations which regulate the teaching are too well known to need repetition here. They have been much improved in recent years by the creation of an "alternative first stage," consisting of a course of chemistry of common things.

An outline of suitable experiments for illustrating the courses, drawn up by Sir Henry Roscoe and Dr. Russell, is issued by the Department for the guidance of science teachers.

Organised Science Schools.—The teaching of chemistry in elementary schools is further influenced by the Science and Art Department by means of "organised science schools." Under the regulations of the Department the scholars of an elementary school (provided that it is not receiving aid from the Whitehall Department on their account) may be formed into an organised science school. For this purpose a course of purely scientific instruction (with the addition of drawing) is laid down. The course includes substantial instruction in chemistry.

For the pupils of such schools who register 250 attendances on the full course, and pass in one subject proper to each year, a capitation grant of 10s. is made in addition to what may be earned at the usual May examinations. Payments are not made for more than four years. The conditions are somewhat different for evening schools.

"Organised science schools" exist in some large towns, as Birmingham, Manchester, Leeds, Brighton, and Middlesborough, the total number in the country being twenty-three.

Statistics.—The following statistics show the number of pupils receiving instruction in chemistry in classes registered under South Kensington, and the number of such who are also studying the subject in public elementary schools.*

	Total number of individuals registered under South Kensington.	Total number of scholars of public elementary schools registered under South Kensington.
Inorganic (theory)	14,241	
Inorganic (practical) ..	6,155	8202
Organic (theory)	1,244	(in 134 schools)
Organic (practical)	926	
Total taking theoretical, inorganic, and organic	15,485	8202

Taking the above figures, in conjunction with those given above, for the teaching of chemistry as a specific subject, we may say that in the public elementary schools of England and Wales there were during the last school-year about 10,000 scholars receiving instruction in chemistry, or about 1 in 364 in average attendance, or 1 in 450 on the total number of children on the register.

In the Appendix more detailed information is given as to the teaching of chemistry in one or two large towns.

Difficulties in the Way of Chemical Teaching in Public Elementary Schools. — Although a satisfactory course of instruction in chemistry might be based on the Code, it is seldom done. Children on leaving the infant schools pass into the standards where elementary science is only an optional subject. The first optional subject must be English, and if a second is taken it is usually geography, and in most schools—as, for example, in those of the Leeds district — there is practically no "elementary science" taught in the first four standards.

When children arrive at Standard V. they may take chemistry as a "specific" subject, but several difficulties are met with, of which the following are the chief:—

1. Between the infant school and the Fifth Standard there is generally a gap of four years, during which the faculties of observation have received no training, and the good beginning made in the infant school has not been followed up.
2. The expense and trouble of preparing experiments. This may, for example, lead to the teaching of physiology (by diagrams only) instead.
3. The smallness of the grant obtainable (4s. for a pass).

The third difficulty is partly overcome by school authorities making the teaching of chemistry as a specific subject preliminary to the classes held under South Kensington, the pupils of which obtain substantial grants; but a difficulty is experienced in co-ordinating the Code Schedule with the South Kensington syllabus, so that pupils on reaching Standard VI. may be only just ready for the South Kensington examinations in the following May. If a pupil is taught chemistry as a "specific" subject in Standard V. for one year, he is usually ready for the elementary stage South Kensington examination, but is not admissible for another year. (If the "Class" subject "elementary science" were taken in Standards I. to IV., as is so desirable, this difficulty would be further increased).

Most boys on reaching Standard VI. leave school, so that they do not take the South Kensington examinations, which is the only way for the school to earn the substantial grants which make science teaching "pay."

In consequence of these difficulties surrounding the teaching of chemistry as a "specific" subject under the Whitehall Department, the greater part of the chemical teaching in elementary schools is forced under the South Kensington Science and Art Department, and school boards are being led to establish higher grade schools, confined to boys who have passed the Sixth Standard and are able to prepare for the South Kensington examinations. They include those boys whose parents are of sufficiently good means to keep them at school after the age of fourteen. Such schools are regarded by many as going beyond the elementary education contemplated in the Education Act of 1870.

Conclusions. — Reviewing the foregoing statements, which I have endeavoured to keep free from merely personal opinions, I am led to the following conclusions :—

1. That the teaching of chemistry in public elementary schools is far from satisfactory in its organisation.
2. That the teaching of chemistry in public elementary schools from its earliest stages in the infant schools to its latest stages in higher grade schools should be under the control of one Educational Department only.
3. That if, as is admitted, the teaching chemistry, adopted at all, should be used as a part of general mental discipline, its organisation and control should not be separated from that of other branches of elementary education, that is to say, it should be conducted under the Whitehall Education Department.
4. That the present inspectorate is ill-adapted for the

* From a return kindly furnished by Major-General Donnelly, Secretary of the Science and Art Department.

supervision and control of chemical teaching, and that special or additional inspectors, suitably qualified, should be appointed.

5. That the Code regulations should be so amended as to give "elementary science" more chance of being adopted as a "class or optional" subject—*e.g.*, by incorporating geography and elementary science as one subject.

6. That the minimum qualifications for science teachers are too low, for, though it is possible for such teachers to inculcate facts, a high standard of scientific knowledge is absolutely necessary for the proper "educative" teaching of the most elementary chemistry.

7. That the peripatetic system is at present the only practicable way of obtaining sufficiently good chemical teaching.

8. That the science teaching in the Universities and University Colleges should be made available for the training of teachers of chemistry in public elementary schools.

9. That, as a rule, chemistry is presented to children in elementary schools in precisely the same way as to undergraduates in the Universities, and that this is the chief cause of unsatisfactory results.

10. That the routine schematic teaching of qualitative analysis which constitutes usually the "practical chemistry" of schools, though pleasing and interesting to the pupils, is most unsatisfactory and uneducative.

11. That there is urgent need of some book, or at least instructions, which shall show how chemistry may be approached naturally and logically from a study of common things and every-day phenomena.

12. That great latitude should be allowed to the teacher to work out a system of the kind indicated, suitable to the conditions under which he works.

13. That the teaching of chemistry as a specific subject cannot be expected to thrive in public elementary schools with only a 4s. grant as against the much larger sum obtainable from South Kensington, and that the Government grant should be awarded, not on individual written examination, but on oral examination combined with general supervision of the character of the teaching.

14. That true specialised technical or professional training in chemistry should not be attempted, but that it should begin not earlier than in recognised state-aided secondary schools, restricted to such scholars as have qualified themselves by a regular and satisfactory course in an elementary school.

Very exaggerated notions exist, and are becoming more and more prevalent, as to what may be properly attempted so far as the teaching of chemistry in elementary schools is concerned. The public do not realise that in the countries where science is most cherished and applied most extensively and successfully to industry (*e.g.*, Germany and Switzerland), the chemical and science teaching in the *elementary* schools is of the most simple and general character, and that the systematic teaching of science for technical purposes begins only in higher schools, polytechnics, and universities. This systematic teaching depends for its success no more on the previous training in science than on the previous training in arithmetic. It demands solely that the previous training shall not have given merely *information*, but that it shall have developed *intelligence*, that it shall have been rational and thorough, and have been administered by good teachers. In this country too much or too little is being attempted, and it is quite a common thing to find boys possessing a large amount of detailed "information" about chemistry, and a certain mechanical aptitude in chemical analysis, who are unable to do a sum in simple proportion or to write their own language correctly.

The most that can be properly aimed at in teaching chemistry in elementary schools is the training of the faculties of observation and of orderly thinking, and the stimulation of the instinct of inquiry, which is the possession of every "uneducated" child. By restricting the teaching to common things and occurrences this can easily be done, and so an interest aroused both in the phenomena of nature and in those involved in industrial operations. In this way there will be created an interest in and appreciation of chemistry amongst the many, and preparation made for the few who can proceed to the highest study of the subject, which alone is *directly* applicable to the advancement of industry.

(To be continued).

OBITUARY.

DR. JAMES PRESCOTT JOULE.

We deeply regret having to put on record the death of one of Britain's most illustrious physicists. Dr. James Prescott Joule died on October 11 in his seventy-second year. Though he wrote neither popular treatises nor separate works on the subjects of his studies, his researches and discoveries—especially that of the mechanical theory of heat—are of such capital moment as to be known to all students of chemistry and physics.

It will not be deemed irrelevant if we remind our readers that Joule never "went up" for any examination, and that throughout his life he worked not for rewards, or even honours, still less from emulation, but from the pure love of truth.

Dr. Joule was one of the surviving pupils of Dalton. He received the Royal Medal of the Royal Society in 1852 for having demonstrated the law of mechanical equivalence of work and heat, and in 1860 the Copley Medal of the Royal Society was adjudged to him, in connection with the same series of researches. In 1872 he was elected President of the British Association, but the state of his health debarred him from attending the meeting at Bradford. Since that time, though an invalid, he has quietly continued his researches.

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—In a letter appearing in Chem. News, vol. lx., p. 184, "Cyclops" says that "it is in your columns *par excellence* that the real grit of an invention is to be ground out." This is a proposition with which I cordially agree, and, feeling convinced that your columns are always open for discussions tending to advance the ends of science, I request your kind insertion of the following explanations, which meet the comments of your correspondent:—

1. I use in the treatment of 1000 gallons of the sewage at Wimbledon about 6½ ozs. of herring brine. This quantity would contain* the equivalent of about 20 grains of propylamine—in the form of salts of the same. It is, however, not for the latter that I claim the disinfecting power, but for new gaseous reagent, resulting from the action thereon of the lime. This reagent I term "Aminol," and its effects have now been repeatedly and conclusively demonstrated. It is quite true that, to the minds of other than scientific men, the action of minute quantities of certain chemicals is startling, but (in the words of your correspondent) "the minds of chemists will not be so easily disturbed."

2. "Cyclops" says:—"It is passing through a second period of juvenility to be fighting the old lime fallacy; a ghost long since laid has raised its head, but this time

* *Vide* Girardin's analysis of herring brine.

cum grano salis." However admirable from a literary point of view this series of metaphors may be, "Cyclops" himself seems to have fallen into the "old lime fallacy," of which he speaks. Dr. Klein found experimentally that lime alone, in the same quantities as those employed in the "Amines" process, was incapable of sterilising. Winter-Blyth failed to sterilise with many times the quantity of lime I use, whilst Richard and Chantemesse in France, and Liborius on Pfuhl in Germany only succeeded in disinfecting by employing about twenty times my proportions. Cyclops evidently was not aware of these researches when he wrote his letter.

3. It is true, that a lime effluent would not be safe in a river; the "Amines" effluent, however, enters the river charged with a powerful disinfectant, which is only diluted *pari passu* with the dissolved organic matter.—I am, &c.,

HUGO WOLLHEIM.

The "Amines" Syndicate, Limited,
101, Leadenhall Street, London, E.C.
October 21, 1889.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

SIR,—Herr H. Wollheim, in his letter of October 9th, points out two errors in my report, which appeared in the CHEMICAL NEWS of September 27th (vol. lx., p. 157) and re-asserts a very serious mistake made in the circular or prospectus of the "Amines" Syndicate.

The quantities of lime herring-brine which I gave were doubtless incorrect, an error which I regret, but which involves no principle.

Mr. Winter-Blyth's researches are disposed of by the statement that the germicide agent is not trimethylamine, but "a new reagent evolved therefrom by the action of the lime." Would it be too much to ask Herr H. Wollheim, in the interests of science, to give the composition and properties of this reagent and to explain the *rationale* of its formation?

If Herr Wollheim and his friends think that all other sludges are a nuisance when *wet*, they have something yet to learn concerning sewage-treatment. There are other processes which not only claim but habitually do produce an inoffensive sludge alike when it contains 90 per cent of water as first drawn out of the tanks and at every subsequent stage. This I know from repeated personal observation, backed by the testimony of scores of independent witnesses. If Herr Wollheim had said we know of no other *lime* process he would have been right.—I am, &c.,

THE WRITER OF THE REPORT.*

VERMILION OR VERMILLION.

To the Editor of the Chemical News.

SIR,—In Spain, where the oldest mercury mines in Europe are situated, the general or common name of the red sulphide of mercury is "cinabrio," but in Castile it is called "bermellon." The "*b*" and "*v*" in Spanish are pronounced so nearly alike that only a well-educated Castilian makes or detects the difference. The "*ll*" has a particular sound in Spanish, which we have endeavoured to retain in the words "million" and "postilion," which are of Spanish origin.

English.	Spanish.
Million.	Millon.
Postilion.	Postillon.
Flotilla.	Flotilla.
Punctilio.	Puntillo.

The introduction of the "*i*" after the "*ll*" is an indication that an endeavour has been made to retain the foreign sound. "Postilion" and "punctilio" have lost one "*l*," but it is still heard in the "*i*"; whilst "flotilla" retains its Spanish orthography, but does not keep the sound of the two "*l*'s," and therefore does not take the "*i*."

The correct orthography of the word should be vermillion, which preserves both the origin and sound of its Castilian equivalent.—I am, &c.,

W. H. DARLING.

Manchester.

* CHEM. NEWS, vol. lx., p. 157.

CONSTANT WATER-BATH.

To the Editor of the Chemical News.

SIR,—I can testify to the efficiency of a constant water-bath similar to the one described by Dr. Davenport in the CHEMICAL NEWS (vol. lx., p. 178). A friend of mine, Mr. G. W. Slatter, A.R.C.Sc., &c., chemist at Saltaire, erected one eight years ago in his laboratory, the condensing arrangement being merely a thick lead pipe, eight yards long, running zigzag upwards, and being open at the top; this being, I think, a great advantage on Dr. Davenport's method.

Mr. Slatter recently informed me that he has only had to re-fill the bath once in eight years, and then only after repairs for leakage, although the bath has frequently been boiling day and night.—I am, &c.,

S. J. SPEAK, A.R.S.M.

Shipley, October 17, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 14, September 30, 1889.

The Application of High Temperatures to the Observation of the Spectrum of Hydrogen.—L. Thomas and Ch. Trépied.—The electric arc affords a certain and relatively easy means of rendering the hydrogen sufficiently luminous for spectroscopic observation, even with the use of great dispersions. On introducing the hydrogen between the carbons the authors observed immediately the appearance of the two lines Hα and Hβ. With a single prism Hα possesses a lustre comparable to that of the metallic rays; Hβ, blunted at its margins, recalled by its constitution the obscure ray, F, of the solar spectrum observed with a dispersion of about twenty prisms. With a dispersion equivalent to that of ten prisms Hα became much broader and blunted at its margins, presenting thus a certain analogy of the corresponding ray of the atmosphere, but still without presenting as marked a maximum; Hβ spread itself out considerably. Lastly, with the great spectroscope of Thollon (about 31 prisms of ordinary flint glass) Hβ is seen indistinctly.

The Connection of the Atomic Weights of Simple Bodies.—M. Delauney.—The author arrives at the conclusion that the atomic weights of the simple bodies are connected with each other by the addition of the square root of a whole number. This number is variable, but always harmonic, *i.e.*, containing no other primary factors than 1, 2, 3, and 5. The chain of atomic weights presents gaps, probably because we do not know all the simple bodies. We remark certain noteworthy places where the links of two bodies become ingrafted: these places correspond to atomic weights following each other in geometrical progression:—24Mg, 48Ti, 96Mo, and 192, probably an unknown body. The following is a specimen of the author's table:—

	Atomic Weight.	Additional Number.
H	1	
Li	7	$\sqrt{36}$
Be	9·25	$\sqrt{5}$
B	11	$\sqrt{3}$

Combinations of Copper Oxide with Amylaceous Bodies, Sugars, and Mannites. New Reagents for Proximate Analysis.—Ch. Er. Guignet.—The solution of cellulose in ammoniacal copper oxide is precipitated by the addition of a large quantity of water, and gives a very definite compound of cellulose and copper oxide, which does not retain ammonia when it has been well washed. If placed in contact with ammoniacal oxide of copper, starch, in its dry state, absorbs copper oxide very readily, so as completely to decolourise the solution. The action is still more rapid with starch slightly moistened. Starch-paste acts in the same manner, but more slowly. Pure water, and even ammoniacal water, only withdraws infinitesimal quantities of copper oxide from the compound. Under these conditions the starch combined with copper oxide is of a deep sky blue and retains ammonia. But if it is heated to 40° in presence of water it loses this ammonia, and becomes of a light green. At 80° the starch passes into the state of paste, retaining anhydrous copper oxide so intimately mixed that under the microscope each grain appeared covered with a blackish grey coating. By a very prolonged digestion with pure ammonia the starch combined with copper oxide is partially dissolved, the solution containing copper oxide and soluble starch. Inuline behaves in an analogous manner. Ammoniacal copper oxide does not throw down any saccharine matter, because the compounds formed by the sugars with copper oxide are very soluble in ammonia. It is not the same with ammoniacal copper (without excess of ammonia). This compound is readily obtained in the crystalline state by adding to ammonia very gradually copper sulphate pulverised and dried at 100°. The liquid heats strongly; it is raised to a boil for some minutes and let cool. Cane-sugar, milk-sugar (and probably the other isomers) do not precipitate ammoniacal copper sulphate. On the contrary, pure glucose (from honey), galactose, &c., precipitate the same reagent in a few moments. The reagent must not be used very concentrated or in excess, as it dissolves the precipitate. Inverted sugar obtained by the action of very weak sulphuric acid upon cane-sugar does not precipitate ammoniacal copper sulphate. It is the same with pure crystalline levulose derived from inuline. But if we add pure glucose to inverted sugar or to levulose the glucosic compound is deposited in a few hours, which seems to show that inverted sugar is a combination and not a mixture of glucose and levulose. Most bodies contained in the decoctions of vegetable matters do not precipitate ammoniacal copper sulphate. This reagent may, in many cases, be employed in preference to lead acetate, neutral or basic. The vegetable acids, the gums, and the pectic matters do not precipitate the ammoniacal copper salt.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iii., August, 1889.

The Periodic Law of the Chemical Elements.—M. D. Mendeleeff.—The "Faraday Lecture."

The Life and Researches of Dmitri Ivanowitch Mendeleeff.—An article founded on Prof. T. E. Thorpe's paper in *Nature*.

Industrial Review.—A selection of patents relating to the chemical arts.

Ochres, Sienna Earths, and Umbers.—G. Hurst.—From the Chem. News.

Aluminium.—Sir H. Roscoe.—From the Chemical News.

The Sophistications of the Vegetable Oils of Commerce: a Critical Examination of the Qualitative and Quantitative Methods for their Analysis.—P. J. S. Girard.—The introduction to a very voluminous paper.

A New Process for Mordanting with Chrome.—G. Saget.—If we pour a solution of potassium bichromate into calcium hydrosulphite with an excess of lime, chromium oxide is at once precipitated. Cloth padded in bichromate and steeped in calcium hydrosulphite becomes green, and attracts all colouring-matters which dye chromium oxide. At 40° the action is immediate.

Industrial Society of Mulhouse.—Session of the Chemical Committee, June 12, 1889.—The Secretary read a paper by M. G. Galland on dyeing with indigo and indophenol in a mixed vat according to the process of Durand and Huguenin. M. A. Schlumberger gave an account of the date when "ungreenable" blacks were first produced at the Mer-Rouge Print works.

Action of Ammonium upon Metallic Magnesium.—H. N. Warren.—From the Chem. News.

The Rapid and Certain Detection of Antimony in Minerals.—A. Johnstone.—From the Chem. News.

Physical Properties of the Graphite obtained from Different Metals after its Elimination by Dilute Acids.—H. N. Warren.—From the Chem. News.

Decomposition of Nickel and Cobalt.—From the Chem. News.

Lixiviation of Silver Ores with Solutions of Hyposulphite and Special Relation with the Russell Process.—Dr. Stettefeldt.—From the Chem. News.

On Potassium Chlorate.—Dr. Hodgkinson and F. Lowndes.—From the Chem. News.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xx., No. 3.

Origin of the Artesian Waters of the French Sahara.—M. Jahacle.—These waters are not as some suppose in filtrations from an interoceanic current, from which they differ in composition, especially by the excess of calcium sulphide, the relatively smaller quantity of chlorides, and the abundant presence of nitrates. They are derived from atmospheric water which takes up salts in filtering through the soil and the rocks.

The Gum of Australia.—Ch. Naudin.—We note in this paper the interesting suggestion to induce in acacias the gummy diathesis by grafting or by inoculation.

Safranine as a New Reagent for Glucose.—The author dissolves 10 centigrms. safranine in 100 grms. water, pours 2 to 3 c.c. of this solution, adds a few drops of the supposed glucosic solution, then 2 to 3 c.c. of soda-lye at 10 per cent, and heats in the water-bath. Between 60° and 65° the safranine is reduced, forming a colourless compound, insoluble in the cold, which gives a milky precipitate. The oxygen of the air regenerates the safranine, forming a red colour on the surface of the liquid.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., Nos. 42 and 43.

These numbers contains no chemical papers.

No. 44.

Report Delivered by M. E. P. Berard, on behalf of the Committee of Chemical Arts, on a Furnace for the Manufacture of Coal-gas, Presented by M. André Coze.—The peculiarities of this furnace cannot be described intelligibly without the accompanying figures.

Journal fur Praktische Chemie.
Vol. xl., Parts 1 and 2.

Derivatives of Meta-toluquinazolin and of Meta-homo-anthranilic Acid.—Stefan von Niementowski.—The author investigates orthonitroparatolunitrile, the corresponding amido-compound, orthoacetamidoparatolunitrile, orthoazoxyparatolunitrile, orthoamidoparatoluylamide, δ-oxymetatoluquinazoline, β-methyl-δ-oxymetatoluquinazoline, toluylazimide, metahomoanthranilic acid, orthoformamidoparatoluylic acid, orthoacetamidoparatoluylic acid, metamethylorthouramidobenzoyl, nitroorthoacetamidoparatoluylic acid, and nitroorthoamidoparatoluylic acid.

Remarks on the Treatise by J. Wislicenus, "On the Geometrical Constitution of the Crotonic Acids and their Halogen Substitution-products. — Arthur Michael. — A controversial paper, not susceptible of useful abridgment.

Fluorine Compounds of Vanadium and of its Nearest Analogues.—Emil Petersen.—There is a very decided analogy between the fluorine compounds of vanadium sesquioxide and of chromium oxide in crystalline form, method of preparation, solubilities, behaviour when heated, and in colour. This shows that vanadium sesquioxide must be placed in the group of analogous basic oxides; those of chromium, iron, manganese, and aluminium. Titanium sesquioxide seems also analogous to this group.

Alloisomerism in the Cinnamic Acid Series.—Arthur Michael and Hunter Pendleton (Third Communication).—According to the experiments of the authors the isomeric relations of the chlorocinnamic acids are quite analogous to those of the corresponding bromocinnamic acids, and the known facts can be understood without assuming a change of position of the halogen.

On the Constitution of Benzol.—Ad. Claus.—A controversial paper. The author points out certain questionable matter in A. Baeyer's second memoir on the reduction of the hydroterephthalic acids. In this memoir Baeyer draws inferences on the constitution of benzol in direct opposition to the conclusions arrived at in his first memoir. Above all he seeks to rehabilitate Kekulé's formula for benzol which he had previously shown to be untenable.

Calorimetric Researches.—F. Stohmann.—In this seventeenth memoir the author, in conjunction with Kleber and Langbein, examines the combustion-heat of benzol and other hydrocarbons. He confirms the accuracy of the thermic value of benzol as already determined. In the solid homologues of benzol the combustion-heat rises by 155·1 cals. on the introduction of each methyl group. If benzol passes into diphenyl owing to the substitution of an atom of hydrogen by a phenyl-group the thermic value rises by 717·0 cals. If in the hydrogen molecule an atom of hydrogen is replaced by phenyl, the combustion-heat of the benzol vapour thus arising is higher than that of the hydrogen molecule by 718·5 cals. The formation of diphenyl from benzol by abscission of two atoms of hydrogen takes place without perceptible evolution of heat. The combustion- and formation-heats of anthracene and phenanthrene are not different. On the conversion of benzol into naphthaline, the combustion-heat increases each time by about 458 cals.

The Action of Hydriodic Acid upon the Crotonic Acids.—Arthur Michael and Paul Freer.—On exactly repeating the experiments of Hemilian the authors obtained not a trace of a liquid addition-product.

NOTES AND QUERIES.

Fluor-spar in Zinc Blende.—Will any of your readers be good enough to let me know—(1) If the presence of fluor-spar in zinc blende has any injurious effect upon the working of the latter. (2) What would be the effect? (3) What would be the remedy?—SPAR.

MEETINGS FOR THE WEEK.

FRIDAY, Nov. 1st.—Physical, 5. "On Electrifications due to the Contact of Gases with Liquids," by J. Enright. "On a New Electric Radiation Meter," by W. G. Gregory, M.A. "On a Physical Basis for the Theory of Errors," by C. V. Burton, D.Sc

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WATER SUPPLY AND SEWAGE: Short Notes for Non-Technical Readers. 8vo. 1s.
London: GURNEY and JACKSON.

PATENTS, DESIGNS, & TRADE MARKS ACT, 1883.

NOTICE IS HEREBY GIVEN that CHARLES FREDERICK HENGST, of 20, Burwash Road, Plumstead, County Kent, has applied for leave to amend the Specification filed in pursuance of the application for Letters Patent No. 13656 of 1888, for "An improved smokeless safety gunpowder."

Particulars of the proposed amendment are set forth in the Illustrated Official Journal (Patents) issued on the 16th October, 1889.

Any person may give notice (on Form G) at the Patent Office, 25, Southampton Buildings, London, W.C., of opposition to the amendment within one month from the date of the said Journal.

(Signed),
H. READER LACK,
Comptroller-General.

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THE CHEMICAL NEWS.

Vol. LX. No. 1562.

THE MANUFACTURE OF THE ALLOYS OF ALUMINIUM IN THE ELECTRIC FURNACE.*

By JOHN H. J. DAGGER, F.I.C., F.C.S.

Although aluminium is one of the most widely distributed of the elements, entering into the composition of nearly two hundred minerals, its oxide, alumina, was regarded as identical with lime until, in 1754, Margraff proved it to be a distinct substance.

In 1807, Davy, so successful with the oxides of the metals of the alkalies and alkaline earths, attempted to decompose alumina by the battery, but failed; and it was not until the year 1828 that Wöhler, by heating the chloride with metallic potassium, first obtained aluminium as a grey lustrous metallic powder, and eighteen years later in globules not larger than pin-heads. From these, with extreme ingenuity, he determined the principal properties of the metal. In 1854, Deville (at that time Professor of Chemistry in the Ecole Normale, Paris), in course of some researches on the chloride, obtained a button of pure aluminium by the decomposition of the chloride with sodium, and on the 4th February in that year read a paper, describing his discovery, before the Academy of Science. As a result, a committee was formed to carry on experiments, 2000 f. being granted to meet expenses. On August 14th, he read a second paper before the Academy, exhibiting several bars of aluminium, and caused a medal of the metal to be struck and presented to the Emperor.

In March of the next year, experiments on a large scale, at the Imperial cost, were instituted at Javel; and on June 18th, Deville presented to the Academy, through M. Dumas, large bars of pure aluminium. These experiments are said to have cost the Emperor 35,000 f. (£1458).

Deville's method, modified in details, is still the chief of the chemical methods of preparing aluminium on a commercial scale, and is dependent on the cost of the metallic sodium and the double chloride of aluminium and sodium, which is the compound used in the most important of the present day processes.

Pure aluminium is a highly lustrous metal, white with a faint tinge of blue in colour. It resists the action of air and moisture, even at high temperatures; is not blackened by exposure to the action of sulphuretted hydrogen or the alkaline sulphides; and is not attacked by fused nitre, nitric, or dilute sulphuric acid. It dissolves readily in hydrochloric acid, or in solutions of the alkalies.

Its density is but two and one-half times that of water. Compared with other metals its density is as follows:—

Metal	Density.	Compared with aluminium.
Platinum	21·5	8·6
Gold	19·3	7·7
Lead	11·4	4·8
Silver	10·5	4·2
Copper	8·9	3·6
Iron	7·8	2·9
Tin	7·3	2·8
Zinc	7·1	2·8
Aluminium	2·5	1·0

In a paper read by Mr. W. H. Barlow before the British Association, 1882, its tenacity is given at twelve tons to the square inch: but weight for weight, it would equal high class steel, or 36 tons per square inch. Its elasticity is almost equal to that of silver. Is ductile, can be drawn into very fine wire, and is almost as malleable as gold. Its thermal conductivity is about two-thirds that of copper; its electrical is given by Deville as eight times that of iron. Its specific heat is 0·22; it melts at 1300° F., but exhibits no tendency to volatilise, even though heated in a carbon crucible in a blast-furnace to high temperatures.

The extreme lightness of aluminium, its power of resisting the action of air, moisture, and sulphuretted hydrogen, give it an advantage over silver, which it equals in tenacity and elasticity, as a material for jewellery and for scientific and astronomical instruments.

The greatest value of aluminium is, as yet, in its alloys, and it is with their production in the electric furnace I propose to deal to-day; and I may remark that the successful application of the intense heat of the electric arc to the production of metals on a commercial scale, marks a new departure in electro-metallurgy, of which we cannot over-estimate the importance, rendering it possible to produce rich alloys of aluminium at half the cost of any other process, and so widening the field of their application to an extent hitherto unknown.

Messrs. Cowles' first experiment was with a very refractory zinc ore, containing silver, which they had failed to reduce in an ordinary furnace. A fireclay tube was taken, filled with a mixture of the crushed ore and charcoal powder, a bundle of electric light carbons inserted in each end, and a current from a small dynamo sent through the mass. In a short time the ore was reduced, but the fireclay tube was partly melted, showing the necessity for a lining that would protect the furnace walls from the intense heat. Powdered charcoal, a very feeble conductor of heat and electricity, was tried, but it was found that after a time it became converted into graphite, thus becoming a conductor; as the smelting proceeded, changing gradually from the inside to the outside, and, as the hot zone expanded, causing loss of energy, and eventually destroying the furnace. Mr. Alfred H. Cowles then suggested soaking the charcoal powder in milk of lime and drying before use—this proved successful, each particle of charcoal being coated with a film of lime which insulates it and prevents electrical conduction between neighbouring particles even after the charcoal is converted into graphite. Messrs. Cowles now found that they had a furnace that would enable them to conduct metallurgical operations at a temperature hitherto unknown outside the laboratory; and after some experiments with corundum, they, acting in conjunction with Professor Mabery, set up the first plant for the production of aluminium bronze, ferro-aluminium, and silicon bronze, at the works of the Brush Electric Co., Cleveland, Ohio, U.S.A. On the 20th of January, 1886, Mr. E. H. Cowles read a paper before the Franklin Institute, describing the electric furnace and a process of making aluminium bronze. The Institute thought so highly of the importance of the discovery that they awarded to Messrs. Cowles the "Elliot" gold medal, the highest honour in the gift of the Institute. The City of Philadelphia awarded them the "John Scott legacy" medal, this being the only instance of the two awards falling to the same inventors.

In 1887, Mr. E. H. Cowles was elected a Fellow of the Royal Society.

The results obtained at Cleveland were so satisfactory, though using only a dynamo of 300 Ampères with E.M.F. of 60 volts., that in 1886 the Cowles Co. commenced the works at Lockport, N.Y., U.S.A. The works at Lockport commenced operations with a Brush dynamo giving a current of 1600 Ampères, with an E.M.F. of 45—50 volts; to this has been added two dynamos each capable of supplying a current of 3000 to 3200 Ampères, with an

* Read before the British Association, Section B, Newcastle Meeting.

E.M.F. of 55 to 60 volts. A fourth dynamo is now building of 3000 Ampères. One striking feature of the Lockport works is the use of water-power, the dynamos being actuated by two powerful turbines, 30 inch diam. = 500 h.p.

The number of furnaces in operation are 14, producing about 300 lbs. of aluminium contained in alloys per 24 hours. Four additional furnaces are now building. I will now describe the English works of the Company at Milton, Staffordshire.

These, the first electro-metallurgical works established in Europe, are situated near Milton station, on the North Staffordshire Railway, with which system they are connected by a siding, and also abut on a branch of the Trent and Mersey canal — thus affording facilities for cheap transit of raw material, coal, and finished products.

The experience at the Lockport works showed conclusively that great economies were to be expected from increasing the size of the furnaces and the strength of the electric currents; but no current of more than 3000 Ampères had been used up to the time the Milton works were planned.

Mr. Cowles then prepared a specification for a dynamo to give a current of 5000 Ampères at 60 volts., and eventually Messrs. Crompton's designs were accepted. This dynamo is of 500 h.p., and furnishes a current of 5000 to 6000 Ampères, with an E.M.F. of 50 to 60 volts. It is said to be the largest machine (at least in regard to quantity of current) in England, and probably in the world. I will not describe this magnificent machine more fully, as it was the subject of a very interesting paper read by Mr. Crompton before the G section of the Association last year.

The boilers supplying steam to the works are of the Babcock-Wilcox type, representing 600 h.p., and are fitted with mechanical stokers; by this means one man can easily attend to the generation of steam for the whole works.

The main engine, used for driving the dynamo only, is a compound condensing horizontal tandem engine, made by Messrs. Pollitt and Wigzell, of Sowerby Bridge, and is well worth noting for its beautiful workmanship. Its motion is, indeed, so silent, that, with your back to it at the moment of starting, you cannot tell whether it is in motion or not. It is of 600 h.p., and is provided with automatic expansion gear; and the centrifugal governor maintains the speed at 76 revolutions. It is needless to say that work of this kind involves rapid fluctuations of load, and as an additional precaution against racing, the engine is fitted with Tate's electrical stop-valve, which stops the engine automatically if the speed exceeds a certain limit. It can also be stopped from various points in the engine and furnace rooms by means of push-buttons connected in parallel with the main circuit leading to the Tate's valve.

The engine has a 23-inch high pressure and a 43-inch low pressure cylinder, the stroke is 5 ft., the average steam pressure being 85 lbs. The fly-wheel is 20 ft. in diameter and weighs 20 tons; it is geared to the dynamo by 18 driving ropes, so that the dynamo makes 5 revolution for each revolution of the engine.

From the dynamo the current is led by copper bars to an enormous "cut-out," calculated to fuse at 8000 Ampères. This is probably the largest ever designed, and consists of a framework carrying 12 lead plates, each $3\frac{1}{2}$ inches broad by $\frac{1}{10}$ inch thick. From this it passes into the furnace rooms; a current indicator is inserted in the circuit, consisting of a solenoid of 9 turns (this was cut out of a cylinder of cast-copper by means of a parting tool, in a screw-cutting lathe). In the solenoid is an iron core suspended by a spring; the movement of this is communicated to two pointers, one dial being placed in the engine-room, the other in the furnace-room. The range of the indicator is such that the entire circle of 360° = 8000 Ampères.

There are two furnace-rooms, each containing 6 furnaces; the first room contains the bronze furnaces, in which is carried on the manufacture of aluminium-copper and silicon-copper; the second is devoted to the production of ferro-aluminium.

The furnaces are rectangular in form, built of fire-brick, the internal dimensions being 60 inches × 20 inches × 36 inches; into each end is built a cast-iron tube through which the carbon electrodes enter the furnace. Each electrode consists of a bundle of 9 carbons, each $2\frac{1}{4}$ inches diameter, attached to a head of cast-iron, for ferro-aluminium, or cast-copper when cupro-aluminium is made. Each carbon rod weighs 20 lbs.

Quite recently it has been possible to obtain carbons 3 inches in diameter, weighing 36 lbs.; these are employed in bundles of 5.

The "head" of the electrode is secured to the copper rods or "leads," which can be readily connected with or disconnected from the flexible cables supplying the current.

Each cable is secured to slides running on omnibus bars of copper overhead, so that it can be brought into position opposite the furnace to be used.

The electrodes are arranged so that it is possible, by means of a handle and screw, to advance or withdraw them from each other in the furnace.

Lining the furnace is the first operation preparatory to smelting. This is done by covering the bottom of the trough with a layer of prepared charcoal.

Oak charcoal is used. This is ground under edge runners, treated with milk of lime, and dried, first in a steam-jacketted revolving drum, and afterwards on a hot iron plate. Each particle of charcoal is thus coated with an insulating film of lime.

The electrodes are now arranged in the furnace, and a "former," consisting of two pieces of sheet-iron connected by stirrups, arched so as to fit over the electrodes, forming a box without top or bottom (the size being dependent on the charge used), is dropped over the electrodes. Prepared charcoal is rammed into the space between the iron sheet and the firebrick walls of the furnace. This done, the charge of ore, mixed with coarse charcoal, and the metal to be alloyed with the aluminium, in form of turnings or granules, is placed inside the iron box, after which this is carefully withdrawn. Some broken pieces of carbon are arranged so as to connect the electrodes and start the current. The charge is then covered with coarse charcoal, and the cast-iron cover, having a hole in the centre for the escape of gases, is lifted into place, and luted so as to prevent the entrance of air.

The commencing current is about 3000 Ampères, gradually increasing to 5000 Ampères in the first half hour. The time occupied by a "run" is about one and a half hours. Soon after starting, the gases escaping from the orifice in the cover take fire and burn with a white flame; this gas consists mainly of carbonic oxide, with small quantities of the hydrocarbons and nitrogen. On the conclusion of the run the furnace is allowed to cool, the melted alloy collecting in the bottom of the furnace; the next furnace ready charged is connected, so that the process is a continuous one, the furnaces being successively charged and connected. A form of furnace in which the metal is tapped from the bottom has given very satisfactory results.

The energy required to produce 1 lb. of contained aluminium depends, of course, upon the grade of alloy, the average being 18 h.p. per hour.

The crude metal from the furnace is then refined and re-melted in a reverberatory furnace; each "run" is sampled, and the percentage of aluminium ascertained by analysis.

The nature of the reaction that takes place in the electric furnace is not very easy to ascertain. The reduction of the ore takes place in an air-tight box, and in presence of an enormous excess of carbon. It may be

assumed that, at the intense heat of the electric arc, the ore melts and gives up its oxygen to the carbon,—

$$Al_2O_3+3C=3CO+Al_2.$$

The presence of copper or iron is immaterial, as the reaction takes place with ore alone; but in absence of the alloying metal the liberated aluminium absorbs carbon and is converted into a carbide.

Prof. Hampe, however, contends that the reaction is in two stages, the first being electrothermic, in which the ore melts; the second electrolytic, in which electrolysis of the molten oxide takes place, aluminium being liberated. Supposing an alternating current is used in the furnace instead of the continuous, and that we have a high number of alternations, from recent experiments with alternating currents we know that very slight, or no electrolytic action occurs; if then we get equal results, it would go to prove that the action is thermic and *not* electrolytic.

An experiment was made by the Cowles Co., using an alternating current.

The furnace used was 48 inches × 12 inches × 24 inches, with current of 900 Ampères with E.M.F. of 50 volts. Alternations per minute, 11,000.

At the end of one and a half hours we obtained 45 lbs. of 4 per cent aluminium bronze.

This investigation was purely of an experimental character, and it cannot be doubted that on the larger commercial scale the result would be more satisfactory.

The results obtained were identical with those given by the continuous current in every way, the resultant slags similar in composition.

The slag from the electric furnace is really only melted unreduced ore, and not a slag in the proper sense of the word. Its approximate composition is:—Al_2O_3, 90; SiO_2, 2·00; Fe_2O_3, 4·00; CaO, 3·9; P, 0·10.

The charcoal from the whole linings, which has been partially converted into graphite, is re-crushed and treated with milk of lime, dried as before, and thus used many times over. The crude metals from the "runs" is re-melted with fluor-spar as a flux, and tapped from the reverberatory furnace into ingots or plates. The refinery slag is put into a revolving drum for breaking into pieces, and then washed to remove carbon — the entangled particles of alloy are thus recovered and are worked up with other charges. These operations are carried out in a separate building—the "reclaiming house."

These works produce about 200 lbs. of contained aluminium per twenty-four hours; the most valuable alloy being aluminium-bronze, which is supplied in grades containing 1¼ to 11 per cent aluminium. To obtain these the rich furnace product containing 15 to 20 per cent aluminium is re-melted and reduced to the desired percentage with metallic copper, and cast in 12 lb. ingots.

(To be continued).

MILK ANALYSIS.

By Dr. BENNETT F. DAVENPORT.

In the discussion of the relative merits of the different methods of milk analysis, which was published in a recent number of the *Analyst*, the many advantages of a simple modification of Wanklyn's method does not, I think, receive its due consideration. This modification, which I have adopted, I have already published in my Annual Report as Milk Inspector for the City of Boston, Mass., 1885, and as analyst to the Massachusetts State Board of Health in their Annual Report for 1886, p. 138. As being now the method generally followed by most of the official milk analysts in New England, a simple description of it may be of interest to others.

The 5 grms. of milk are weighed off in a large flat-bottom platinum capsule of full 2½ inches diameter on the bottom, and about 3 inches across the top. The ½-inch high side turns up from the bottom, not with a sharp angle, but slight rounding, this being about the curve with which the milk runs up the rim of the capsule drawn by capillarity. The milk, in drying down, does not thus form any thicker deposit at the angle of the side than elsewhere upon the about 5 square inches of bottom surface of the capsule. This relatively large amount of surface, one square inch to each grm. of sample taken, causes each inch to be covered with only a little over a single grain of dried milk solids. The deposit is therefore so very thin as to be readily exhausted of its fat in its subsequent treatment with boiling petroleum naphtha. When using such small dishes as were originally proposed by Wanklyn the residue would be so thick, that is about three times, as would naturally render any such rapid method of extraction as I employ impossible, as the English analysts have learned. Each capsule has its serial number engraved upon it, and they are made to weigh a little over 25 grms. each, that the bottoms may be stiff enough to remain perfectly flat, a matter of very great importance. They are also made to differ from each other only in the second and third places of decimals, so that only those weights have to be changed in many weighings, which is a matter of no little saving of labour where many score of weighings are to be made each day. A table of their weights is kept within the case of the scales. These capsules containing their samples are placed upon a constant-level closed-top water-bath of the peculiar construction described in the *Journal of Analytical Chemistry*, Vol. iii., Part 3, p. 269. This will hold 25 capsules at a time. Here, being surrounded by an atmosphere not already nearly saturated with moisture, as would be the case if they were upon a water-bath with openings on its top, they quickly evaporate to apparent dryness. They are then transferred for their final drying to a constant weight to one of Weisnegg's large porcelain-lined air-baths, regulated to the constant temperature of 105° C. Here they are dried in about half an hour, when they are cooled in a desiccator and each weighed immediately upon being taken out to guard against their rapid gain in weight from exposure to the air. Replaced upon the closed-top water-bath, the capsule is filled from a wash-bottle with petroleum naphtha of the quality of the benzine of the "U.S. Pharmacopæia," revision of 1880. This, unlike ether, will dissolve out neither milk-sugar nor lactic acid from the dried milk-solid residue. Moreover, one gallon of it costs but as much as one pint of ether would, which is a matter of some little consequence to one like me, who has had to use about 100 gallons of it in milk analyses during the past five years.

The naphtha in the capsule, after being allowed to boil down about one-half, is decanted off against a rod into a basin to guard against the remote possibility of some flakes of milk residue being poured off with it. Replaced upon the bath, the capsule is refilled with naphtha. This boiling up and decanting off is repeated three to four times, when, after the last one, the outside of the capsule is washed off with naphtha played upon it from the wash-bottle to prevent any residue of fat being left there. The capsule then finally replaced upon the bath to dry off the naphtha, is then cooled and weighed as before, the butter being rather determined from the loss of weight in the solids than by the weight of the evaporated washings.

The ash is made by ignition of the capsule over a one-inch wide Bunsen lamp, which thus gives so wide a flame as not to require a heating to a high temperature at one point, and thus a possible loss by the volatilisation of the potassium chloride. The milk-sugar I determine by the use of a Soleil-Ventzke saccharimeter in the same manner as has now been several times described in the journals by Drs. Wiley Vieth and others. The other ingredients which reduce copper in Fehling's solution, are not thus reckoned as sugar, by which the apparent

amount of albumenoids present, which are obtained by difference, would be diminished.

The peculiarities of my modification is, then, the use of an evaporating capsule of such a very large relative area as will leave the residue thin enough to be readily exhausted by the boiling naphtha. Thus, a diameter of 2½ inches in the capsule will do for 5 grms. of better than average quality of milk, with a surety that there will not be as much as one-tenth of one per cent of fat left as a maximum error. And surely this is fine enough for all commercial work, and it is much to be doubted if much which affects to be more accurate by a decimal than this is really so. The method, as involving no transfer of substance, cannot well be made more simple for the determination of total solids, fat, and ash. When the average life of such an evaporating capsule under reasonable usage is considered, it cannot well be cheapened, although the outlay for a kilo. of platinum for 40 capsules like mine does, it is true, involve an original expense of nearly 400 dollars. The shape of my capsules makes possible completeness of extraction with the solvent used, and the construction of the closed water-bath hastens the process in no small degree.—*Journal of Analytical Chemistry*, Vol. iii., Part 3, July, 1889.

RAPID ESTIMATION OF FAT IN MILK.

By A. W. STOKES, F.C.S., F.I.C. (Public Analyst).

IT has become very much the custom of late with those who have to analyse large numbers of milk samples to determine only the total solids and the specific gravity. From these the fat can be calculated with great accuracy, thanks to the very excellent formulæ of Messrs. Behrend, Morgen, Fleischmann, Clausnitzer, Mayer, Hehner and Richmond. In cases, however, where the milk has become sour, or where preservatives have been added, this calculation is either impossible or misleading. Other cases arise where the results of the calculation do not agree with one's experience of the relative proportions of the sample's constituents. In such cases it is usually necessary to resort, for exact determination of fat, to the Soxhlet, Adam's paper coil, or the plaster-of-paris method. All these need many hours for a single determination, as well as special apparatus and attention.

In the CHEMICAL NEWS, vol. lviii., p. 197, was the following full translation of an abstract from the *Zeitschrift fur Analytische Chemie*, Vol. xxvii., Part 4 :—

"Dr. Werner Schmid takes a test-tube of about 50 c.c. capacity, graduated in tenths of a c.c., introduces 5 c.c. of cream or 10 c.c. of milk, accurately measured, adds 10 c.c. of strong hydrochloric acid, boils, with shaking, until the liquid turns dark brown, cools by placing the tube in cold water, adds 30 c.c. of ether, shakes round, lets stand, measures the volume of the ethereal solution, draws off 10 c.c. with a pipette, evaporates down in a weighed porcelain capsule on the water-bath, and finally in an air-bath at 100°. He then weighs and calculates for the original quantity of the ethereal solution. If the process has been rightly conducted the ether separates from the aqueous solution clear, without the slightest turbidity. The ethereal solution, as it flows out of the pipette, should not show any watery drops. The results are perfectly accurate, and differ from each other and from the ordinary gravimetric methods by less than one-tenth per cent. The operation requires at most fifteen minutes"

Neither in the original nor elsewhere could I find any further particular, or any evidence of the working of this method. I have now for just one year tried this method on some hundreds of samples of milk, both in competition with other methods and against the calculated results obtained from sp. gr. and total solids. For this last I have used the admirable table of calculations of Messrs. Hehner and Richmond in the *Analyst*, vol. xiii., p. 26.

In a paper contributed to the *Analyst* of Feb., 1889, I showed the comparative results of this method and some others; but as the method of working there described is not the best, the results there recorded are not by any means as close as they should be. The method now adopted is as follows :—

Into special tubes (to be obtained of Messrs. Townson and Mercer), which are partly graduated up to 50 c.c., pipette 10 c.c. of the milk, if fresh, and then pour direct from its bottle some HCl roughly to the 20 c.c. mark. If the milk is a sour sample, weigh out 10 grms., and, with a small wash-bottle containing strong HCl, wash the milk into the tube till it is full to the 20 c.c. mark about. Now boil the mixture with frequent shaking till it turns brown. Merely heating it to the boiling point of water by immersion in a water-bath is not sufficient. Leave for about three minutes to stand; the colour will darken considerably, while thus standing, without further heat. Cool by immersion in water; fill up roughly to about the 50 c.c. mark with ether. It is not necessary that the ether should have been previously washed with water unless it contains more than 3 per cent of alcohol. Cork the tube and shake the mixture for half a minute; let settle for five minutes. Accurately pipette off 20 c.c. of the supernatant ethereal solution into a tared dish, evaporate off the ether, dry in air-bath, and weigh the residual fat. It is advisable to take at least 20 c.c. of the ethereal solution, so as to avoid the errors of high multiplication. It is perfectly easy to pipette off accurately 20 c.c. of the ethereal solution; the presence of fat in the ether prevents the difficulty that is found in pipetting off ordinary ether. Now notice how many c.c. of ethereal solution are left in the tube. Here there is sometimes a slight difficulty, since above the sharp line that separates the brown mixture of HCl and milk from the colourless ethereal solution sometimes there floats a fluffy narrow stratum of casein. If, however, three quarters of this stratum be assumed to be ether a correct reading will be made. From the whole quantity of ethereal solution originally present the percentage of fat in the milk is now calculated.

The whole process, doing at the same time a number of samples, need not take more than twenty minutes. Its accuracy is not excelled by any other process; the process is simple; the reagents are those found in every laboratory; almost all the ether and the HCl can be recovered if thought worth while; the only special apparatus needed is a cheap calibrated test tube.

The HCl and the milk in the process should not be boiled together more than two minutes, else the ether will take up a caramel-like substance. Very highly watered milks do not turn a dark brown because of the small amount of milk-sugar present; while condensed and sugared milks become almost black.

An example may show the calculation required.

10 c.c. of a milk having the sp. gr. 1031 and giving 12 per cent by weight of total solids, when treated thus, gave, in 20 c.c. of ethereal solution, 0·277 grm. of fat. There were left in the tube 6·5 c.c. of ethereal solution, making a total of 26·5 c.c. Then—

$$\frac{0{\cdot}277 \times 26{\cdot}5}{2}$$

=3·67 per cent in 100 c.c. of the milk. Dividing this by the sp. gr., 1031, we get 3·55 per cent by weight of fat in the sample. Calculating from the sp. gr. and total solids, the fat should be 3·54 per cent.

To show the average results obtained I give the results on 12 samples of milk. These are not selected in any way except to show how the method answers both with rich and poor milks (see Table, next page).

These are not made-up milks, but those received in the ordinary way from various parishes under the Adulteration Act. The difference, with ordinary care in working, between the observed fat and the calculated fat never comes to the first decimal point in the percentage.

Sample.	Total solids.	Fat found.	Fat calculated.
No. 1 ..	15·64	6·54	6 57
,, 2 ..	13 60	5·16	5·14
,, 3 ..	11·68	3·81	3·82
,, 4 ..	11·46	3·50	3·52
,, 5 ..	11·40	3·26	3·25
,, 6 ..	11·40	3·25	3·25
,, 7 ..	11·30	3·14	3·16
,, 8 ..	9·86	2·87	2·88
,, 9 ..	11·30	2 60	2·60
,, 10 ..	10·20	1·94	1·97
,, 11 ..	8·90	1·86	1·85
,, 12 ..	9·61	1·33	1·32

Like most processes, it requires a little experience before exact results are attained. But the personal equation does not influence the method, for some of the many samples were done by my assistant, Mr. E. Michael (to whom I owe many thanks for care shown), and then repeated by myself, with the same results. In many cases part of the operation was done by one and the rest by the other; results came out just the same in agreement with the calculated fat. To ensure accuracy for the calculated at the total solids were dried over the water-bath and then in the air-bath, using flat-bottomed or glass dishes of 2½ inches diameter, and always taking about 5 grms. of the milk.* The sp. gr. was very carefully taken at 60° F. either by the Westphal balance or by the sp. gr. bottle.

In milk the fat is undoubtedly in some way held by the casein; in this process the strong boiling HCl destroys the casein and liberates the fat; the ether afterwards dissolves the fat. This ethereal solution is always slightly acid, but on evaporating off the ether the acid is also got rid of and only pure fat remains. Analysis of several samples of this fat shows it to be free from any other of the milk constituents. I am doubtful if any fat at all remains in the mixture of milk and HCl. If there be any, it must be exceedingly minute in quantity, and cannot influence the results.

ANALYTICAL STUDIES ON PHOSPHODODEKAMOLYBDIC ACID, THE CONDITIONS OF ITS FORMATION, AND ITS SEPARATION AS AN AMMONIUM SALT.

By Dr. FRANZ HUNDESHAGEN.

(Concluded from p. 203).

Appendix.

1. *Remarks on Finkener's Method of Direct Weighing of the Phosphomolybdate.*

As compared with that of Hehner, the method proposed by Finkener for the direct weighing of phosphomolybdate deserves the preference, since it avoids the following defects, which are inherent in the process of the former chemist. It dispenses with the hazardous washing of the precipitate with water (or with alcohol at 45 per cent), the tedious and repeated evaporations of the ammoniacal solution, and the troublesome drying of the residue, which is very sensitive to any elevation of temperature. Hence it is at once more trustworthy and more expeditious. The objection raised by Hehner, that the phosphomolybdate is easily reduced on drying, may be set aside if the following precaution is used:—The precipitate, after washing with a 5 per cent solution of ammonium nitrate, slightly acidulated, is dissolved in warm dilute ammonia. If the precipitate, as it is done by Finkener, is washed off the filter, the solution, as it contains fibres of paper, must not be evaporated until it has been filtered once more. The filtrate is received in the capsule and evaporated along with the washings until the liquid retains only a faint odour of ammonia, dilute nitric acid is added for the complete precipitation of the phosphomolybdate, and again evaporated as Finkener directs. The thick residue is heated over a wire gauze, at first gently and afterwards, when it ceases to froth, more strongly, until the ammonium nitrate is entirely expelled. The temperature of the crucible may reach 160°—180°. When a watch-glass, placed over the crucible, does not become coated after half a minutes' exposure, all the nitrate is volatilised. The yellow pulverulent residue is triammonium phosphomolybdate, free from moisture and acid, and after drying in the desiccator it is weighed in a covered capsule. It contains, according to Finkener, 3·794 per cent P_2O_5—

$$\left(=\frac{1}{26{\cdot}352}\right).$$

The formula requires 3·78 per cent—

$$\left(=\frac{1}{26{\cdot}46}\right).$$

The percentage of P_2O_5 in the residue is regularly rather less. The proportion of P_2O_5=3·72 per cent—

$$\left(\frac{1}{26{\cdot}90}\right)$$

can, indeed, not be regarded as quite decisive, on account of the very small quantities employed; but from a number of weighings there appears a rather lower value, a mean of 3·753 per cent—

$$\left(=\frac{1}{26{\cdot}65}\right),$$

which borders very closely on the demands of theory.

2. *Methods for the Indirect Measurement of the Ammonium Phosphomolybdate.*

The following indirect methods result from the experiments above given:—

Saturation with Alkali.—a. The precipitate, after being washed with a cold, neutral 5 per cent solution of ammonium nitrate, is placed in a beaker along with the filter, and diffused as uniformly as possible by stirring with a glass rod. In order that there may be no subsequent loss of ammonia, the volume of the water must not be less than 30 c.c. to 0·010 grm. P_2O_5. A few particles of phenolphthalein are added, and standard soda-lye is run in, constantly stirring till the liquid takes a decidedly red colour. When all the precipitate is dissolved we titrate rapidly back with nitric acid until all colour has disappeared. If in consequence of a slight reduction there remains a bluish colouration, a transition from reddish to greenish blue marks the limit of neutrality.

For neutralising the mol. of ammonium phosphomolybdate there are required 23 mols. NaOH.

1 c.c. of a decinormal soda-lye (=0·008 grm. NaOH) represents 0·016322 grm. ammonium phosphomolybdate, 0·00061739 grm. phosphoric acid, and 0·015026 grm. molybdic acid.

b. The precipitate, freed from acid by washing, is, as above, distributed in water and dissolved in a measured volume of dilute soda or sodium carbonate. The liquid is tinged with a trace of phenolphthalein, and titrated with decinormal acid until the colour disappears. Another equal volume of the alkaline liquid is measured and titrated with the same acid. Of the excess of acid consumed in the second experiment, 23 mols. represent 1 mol. ammonium phosphomolybdate.

The author has not tried this latter method.

Precipitation from a Neutral Solution by Nitric Acid.—The washed precipitate is dissolved in ammonia, the liquid mixed with ammonium nitrate (about 10 per cent), accurately neutralised, and titrated with nitric acid until complete precipitation is effected, using the precautions laid down above; or the neutral solution is thrown down with

* The use of the air-bath for drying the total solids is essential if results are needed in reasonable time, taking care, however, that the temperature never exceeds 100° C.

an excess of standard nitric acid, filtered, washed with solution of ammonium nitrate, and the excess of nitric acid is determined in the filtrate. The difference represents the acid consumed in precipitation. About 26 mols. precipitate 1 mol. ammonium phosphomolybdate (see section 4).

One c.c. $\frac{n}{10}$ nitric acid = 0·0126 grm. NO_3H, represents 0·01444 grm. ammonium phosphomolybdate, 0·00054616 grm. phosphoric acid, and 0·0132923 grm. molybdic acid. —*Zeitschrift fur Analytische Chemie*, vol. xxviii., p. 141.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING SEPTEMBER 30TH, 1889.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P., Professor of Chemistry at the University of Oxford;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law, Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A., *Water Examiner, Metropolis Water Act*, 1871.

London, October 9th, 1889.

SIR,—We submit herewith the results of our analyses of the 175 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from September 1st to September 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

The whole of the 175 samples examined were found to be clear, bright, and well filtered.

It will be seen that during the month of September the supply of water to the Metropolis has fully maintained the satisfactory character taken note of in our two previous monthly reports.

The supply for the past three months has been characterised by presenting a notable uniformity of composition throughout; as is especially shown by a comparison of the results furnished by the water distributed by the Companies taking their supply from the Thames.

Thus the several mean amounts of oxygen required to oxidise the organic matter present in a gallon of the Thames-derived water, were found to be 0·040, 0·037, and 0·34 of a grain, in the months of July, August, and September respectively.

Similarly the mean amounts of organic carbon present in the successive months' supplies were found to be 0·137, 0·138, and 0·138 part respectively in 100,000 parts of the Thames-derived water; while the maximum amount of organic carbon met with in any single sample examined in July was 0·153 part, in August 0·151 part, and in September 0·148 part in 100,000 parts of the water, these maximum proportions of organic carbon corresponding as nearly as may be to but just over a quarter of a grain of organic matter per gallon.

Having regard, however, to the seasonal fluctuations in composition, for the most part indeed within a very narrow range, to which river-water is liable, a continuance of such low and uniform results as those above recorded is hardly much longer to be expected.

We are, Sir,
Your obedient Servants,
WILLIAM CROOKES.
WILLIAM ODLING.
C. MEYMOTT TIDY.

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

(Continued from p. 207).

APPENDIX.

I. *Chemistry in the London Board Schools.*†

THE teaching of chemistry in the London Board schools calls for special remark, in view of the comprehensive scheme of "systematised object lessons, embracing in the six school years a course of elementary instruction in physical science, and serving as an introduction to the science examinations which are conducted by the Science and Art Department." This system has been in vogue for some years and constitutes the optional subject—"elementary science"—of the Code. It is continuous with the object lessons of the infant schools, and bridges over the usual gulf between these and the "specific" science subjects. The following is a model scheme suggested by the School Management Committee of the London School Board:—

Standard I.

Extension of the object lessons in the infant school, with simple illustrative experiments.

Standard II.

Comparison of different plants or animals.
Ordinary phenomena of the earth and atmosphere.
Substances of domestic use.

Standard III.

Simple principles of classification of plants and animals.
Further phenomena of the earths and atmosphere.
Substances used in the arts and manufactures.

Standard IV.

More complete classification of plants and animals, with typical examples.
The three forms of matter familiarly illustrated.

Standard V.

(*a*). Animal and plant life, with the most useful products;

or,

(*b*). More definite notions of matter and force illustrated by simple machinery or apparatus.

Standard VI.

(*a*). Animal and plant life, with special reference to the laws of health;

or,

(*b*). The commonest elements and their compounds.
The mechanical powers.

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe. Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

† For this information I am much indebted to Dr. J. H. Gladstone, F.R.S.

Standard VII.

(*a*). Distribution of plants animals, and the races of mankind;

or,

(*b*). Light, heat, and electricity, and their applications.

The scheme is adopted wholly or partially in a considerable number of London Board schools. It is encouraged by the Board providing the rarer objects and offering a museum cabinet to any school in which a good commencement of a collection has been made. It will be seen that the course of instruction embodies a considerable amount of elementary chemistry.

The teaching of chemistry as a specific subject calls for no special remark. It is only adopted in ten schools, and no special teachers are provided.

The systematic teaching of mechanics ("in a large sense") by four peripatetic demonstrators is a very important feature in London Board schools. "The science demonstrator gives a lesson fortnightly to the boys in the fifth and higher standards, the lesson being illustrated experimentally by specimens and apparatus carried from school to school." This system is being widely adopted in the London School Board district, but it is scarcely yet beyond the experimental stage. Its prevalence accounts largely for the small amount of chemical teaching, but this is also attributed to the fact that chemistry is not of the same relative importance in London arts as in those of other large towns.

At the annual examination in 1888, 341 pupils passed in chemistry as a specific subject out of an average of 51,214 boys and girls in attendance on one or other of the fourteen "specific" subjects, or a total of about 420,000 children on the school registers.

In the evening schools chemistry is taught on the lines of the South Kensington syllabus, but only to a very slight extent, the number in attendance not exceeding 100 in 1887—1888.

In the pupil-teachers' schools chemistry is also taught according to the syllabus of the elementary or alternative elementary stage of South Kensington.

II. *Chemistry in Birmingham Board Schools.*

In the thirty-four Birmingham Board schools, with average attendance of 38,000, all boys receive instruction in "Elementary Science" in Standards V. and VI. Thus 2700 boys learn mechanics, 550 magnesium and electricity. 2200 girls learn portions of chemistry and physiology under the name of Domestic Economy. The instruction is given by a peripatetic demonstrator and four assistants, who give a lesson once a fortnight to each school. The lesson is recapitulated by the class-teacher, and the children reproduce it in a composition.

The teaching of chemistry as a distinct subject begins in a central Seventh Standard school, in which there are 200 scholars, with a head-master and five assistants.

In May, 1887, at the South Kensington examinations, 110 scholars were presented in theoretical inorganic chemistry, of whom only seven failed; in practical inorganic chemistry 112 were presented, 17 failed.

III. *Chemistry in Manchester Public Elementary Schools.*

(From a return issued by the Manchester Branch of the National Association for the Promotion of Technical Education).

Day Schools:—

Chemistry as a "specific" subject.—

Board schools	159 scholars.
Voluntary schools	5 ,,
Total	164

Chemistry as a science subject (under South Kensington).—

	Inorganic (theory).	Inorganic (practical).	Organic (theory).	Organic (practical)
Board schools ..	447	424	40	40
Voluntary schools	23	—	—	—
Total	470	424	40	40

Evening Schools:—

Chemistry as a science subject (under South Kensington).—

	Inorganic (theory).	Inorganic (practical).	Organic (theory).	Organic (practical).
Board schools ..	262	206	39	28
Voluntary schools	47	23	—	—
Total	309	229	39	28

Probably not less than 1000 pupils are receiving instruction in chemistry in these public elementary schools.

The teaching is in higher-grade schools, and also by means of peripatetic demonstrators.

There is laboratory accommodation provided by the Manchester School Board for 184 students; by the Salford Board for 70.

IV. *Chemistry in the Grant-earning Public Schools of Scotland.**

So far as science-teaching is concerned, the provisions of the Scottish Education Code are similar to those of the English Code.

Very little "elementary science" appears to be taught, and in chemistry, as a specific subject, only 350 scholars obtained grants in 1888—1889.

A considerable amount of teaching is done in connection with South Kensington, but I have been unable to obtain exact statistics.

There are no higher-grade Board schools in Scotland, as the Scotch School Boards have the control of many old-established secondary schools, such as the High Schools of Edinburgh and Glasgow. In some of these efficient instruction is given in special sciences.

The Technical Education (Scotland) Act of 1887 is so far a dead letter.

V. *Teachers of Chemistry in Public Elementary Schools and their Training.*

The following classes of teachers are recognised by the Education Department:—

Pupil teachers, assistant teachers, provisionally certificated teachers, certificated teachers, teachers of evening schools, and, by the Science and Art Department, science teachers.

It has already been stated that teachers of "elementary science" in the first four standards need not have passed any examination in science, nor are the inspectors enjoined to inquire particularly into the previous training of such teachers.

As to chemistry as a specific subject, the inspectors are instructed that it will be desirable for them to ascertain that the teacher has given proof of his fitness to teach by having acquitted himself creditably at a training college or at some other public examination.

The chemistry teaching in training colleges† is under the regulations of South Kensington. The students, unless possessing previous knowledge of the subject, are intended to have two years' training, of which instruction in practical chemistry and the performance of "the more important and characteristic of the experiments" are a necessary part. In December of each year an examination is held, on the results of which all payments on behalf of instruction in science in training colleges are made. This examination is based on the syllabus of the ordinary May examinations; but the standard is some-

* I am indebted to Professor Carnelley for information on this subject.

† *I.e.*, colleges for teachers in public elementary schools only.

what higher, and special questions are set on the method of teaching. Students who pass on the advanced paper or in honours are registered as qualified to earn payments on results.

At Christmas, 1887, 297 students in training colleges presented themselves for this examination in inorganic chemistry, of whom 76 passed in the first division, 172 in the second division, and 49 failed. In practical chemistry, of 190 candicates, 47 obtained a first class, 96 a second class, and 47 failed.

Any person over eighteen years of age approved by the inspector may become a teacher in evening schools.

The simplest qualification for a teacher of chemistry as a science subject under South Kensington was, until recently, the obtaining of a second class in the advanced stage at the May examinations in that subject. This is now raised to a first class. The other qualifications considered equivalent by the Department need not be enumerated, except the most important one, viz., that the teacher has been trained at the Normal School of Science and Royal School of Mines. For details of the curriculum reference must be made to the Science Directory.

Certain grants and privileges are allowed to science teachers who have proved themselves specially meritorious. These are briefly—

(*a*). Payment of railway fare and £3 to attend a free summer course of lectures at South Kensington; or,

(*b*). Free admission to the classes of the Normal School of Science, railway fare, and 21s. or 30s. per week whilst in attendance; or,

(*c*). Part payment (¾ for day classes, ½ for evening classes) of fees for classes taken at university colleges by selected teachers; or,

(*d*). Payment of expenses of a teacher taking a group of towns or villages; or,

(*e*). Admission of qualified teachers to classes at South Kensington at a fee of £1 for each subject.

In the session 1886-7 there were at the Normal School of Science twenty-four teachers in training taking chemistry, in addition to a larger number of regular students, who will become eventually science teachers. Forty-seven science teachers attended the summer course in chemistry.

Forty-two teachers were selected to attend classes at university colleges, of whom only a part took chemistry.

In addition to the above methods of training teachers, school boards may themselves institute special classes. Thus in Leeds there has been during the past year a class for the instruction of elementary teachers and one for pupil teachers in theoretical and practical chemistry. Instruction was given by the science demonstrator to the School Board, and the attendance was 30 in the first class and 12 in the second. It would be very difficult to obtain complete statistics of the amount of this kind of teaching that is in operation throughout the country, but it does not appear to be very general.

VI. *The Teaching of Chemistry in Evening Schools under the Education Department.*

The chief points in which the administration of evening schools differ from that of day schools are as follows:—

1. No pupils may be presented for examination below the third standard.
2. In the third or fourth standard the first subject additional to the three R's must be English, and, if a second be taken, it must be geography or elementary science.
3. Above Standard IV. scholars are unrestricted in their choice of additional subjects.
4. A fixed grant of 4s. is made on the average attendance if the class has met not less than forty-five times and of 6s. if not less than sixty times.

A grant of 2s. is made for every pass in an elementary or additional (*i.e.*, class or specific) subject.

The total number of scholars on the register of evening school in 1887-8 was about 50,000, of whom about two-fifths were in Board schools and three-fifths in Voluntary schools. One-seventh of the scholars were under fourteen years of age, and one-twentieth twenty-one and over. Nearly four-fifths were qualified for examination. About 1200 passed in two additional subjects (*i.e.*, they may have taken a science subject).

More detailed returns are not published, but probably it is safe to say that less than 500 evening scholars took chemistry as a specific subject. This shows that the teaching of chemistry to evening scholars is almost entirely under the Science and Art Department.

VII. *Recommendations of the Royal Commission on Technical Instruction (Report 1884) affecting Chemical Teaching in Public Elementary Schools.*

The Commissioners recommend—

(*a*). That science be given a more favourable position under the code by a reduction of the number of "class" subjects to two in the lower divisions of schools, one of which shall be elementary science, including geography.

(*b*). That school boards have power to establish, conduct, and contribute to science classes for young persons and artizans under the Science and Art Department.

(*c*). That the teaching under South Kensington be made more practical in the higher stages and be subject to more thorough inspection; that payment of fees be not necessarily demanded from artizans, and that the building grants be not limited to £500.

(*d*). That the teaching of science in training colleges be made more efficient and subject to better inspection, and that greater facilities be given for the students to pass on to the Normal School of Science, or other place for higher scientific instruction.

(*e*). That secondary, "modernised," and technical schools should be established out of ancient endowments and by contributions from "local authorities."

VIII. *The Technical Education Bill (1889) and the Teaching of Chemistry in Public Elementary Schools.*

This Bill, introduced by Sir Henry Roscoe on behalf of the National Association for the Promotion of Technical Education, would, if passed in its present form, make the following changes:—

(*a*). School boards or *local authorities*, or *both*, would be enabled to establish day or evening classes and provide laboratories, apparatus, and collections, &c., for the teaching of chemistry in public elementary schools *and to maintain them from the "local rates,"* with aid from the Education or Science and Art Department, or both, under conditions to be defined by special minutes of the departments. Admission to such classes *would not necessarily be restricted to children above the fourth standard*, although power is given to impose an entrance examination in reading, writing, and arithmetic.

(*b*). School boards or local authorities might also contribute directly or by payment of the fees of deserving students, or by means of scholarships to the aid of the teaching of chemistry *in any elementary, secondary, or technical school or in a college*, and grants in aid would be obtainable by schools from the Science and Art Department.

(*c*). Chemical instruction provided under this Act in public elementary schools would be under the inspection both of the Whitehall and South Kensington inspectors.*

* The important innovations are italicised.

The Technical Education Bill would thus affect the teaching of chemistry favourably as regards secondary and higher instruction, enabling the school boards and local authorities to make direct contributions to mechanics' institutes, technical schools, grammar schools, and colleges, as well as to their own technical classes in elementary schools. It is difficult to say how far it would affect the teaching of chemistry in *bonâ fide* elementary schools; but it seems to aim either at encouraging the optional subject, elementary-science, and the specific subject, chemistry, and increasing the grants on them indirectly, or at enabling children to receive chemical instruction of the South Kensington type in the early standards irrespective of the three R's. If the Bill passes in its present form, there will apparently be three ways of taking chemistry in an elementary school, viz., (1) as a specific subject under the Whitehall Department; (2) as a science subject under South Kensington; (3) as a technical subject under both. The educational aim is the same in all three cases, and it seems a great pity that the small amount of simple science teaching that is required for children in legitimate elementary schools should be so complicated in administration. It would seem that a simple alteration of the code is required to give a proper basis for technical instruction, and that a technical or secondary instruction Bill would be more fittingly limited to technical and secondary schools.

(To be continued).

NOTICES OF BOOKS.

Chemical Technology; or, Chemistry in its Applications to Arts and Manufactures. Edited by C. E. Groves, F.R.S., and W. Thorp, B.Sc., with which is incorporated "Richardson and Watts' Chemical Technology." Vol. I. "Fuel and its Applications." By E. J. Mills, D.Sc., F.R.S., and F. J. Rowan, C.E. London: J. and A. Churchill.

We have here a book not merely valuable, but admirable, from the patience and erudition shown by the authors in collecting the materials, as well as from their judgment in elaborating the vast mass of matter which has been in their hands. Nor must we overlook the number, the appropriateness, and good execution of the illustrations.

As regards the history of the work, its basis is a German treatise well known as "Knapp's Technology." An extended, and English, edition was brought out by Richardson and Ronalds, and was again much enlarged and in great part re-written by Richardson and Watts.

The present work is, however, necessarily to a great extent a new departure, and is divided into a number of sections, of which the present volume, on "Fuel and its Applications," forms the first. The authors here discuss the subject generally, the special employment of fuel in the various chemical arts being reserved for subsequent volumes. The justice of opening a work on chemical technology with a study of the means of producing or applying heat will be apparent if we remember that of old the chemist was termed the "philosopher *per ignem*."

The authors, after introductory generalities on fuel, consider in succession wood, peat, coal, the effect of heat on fuels, wood, charcoal, coke, peat-distillation, artificial fuel, gaseous combustibles, liquid fuel, minor fuels, theory of heat, flame, the application of fuel, domestic heating, heating by hot air, hot-blast stoves, heating by water and steam, the application of fuel to vaporisation, evaporation, distillation, drying, bakers' ovens, brick and porcelain kilns, furnaces, gas furnaces, the practical effect of fuel, concluding with analytical tables of various kinds of coal and other fuel, and with an appendix on coal-washing.

In the account of areas of coal in different countries, and in the remarks on its quality, we find certain omissions which are to be regretted. There is no mention whatever of the coal-fields of Natal, and of other parts of South Africa, although these are understood to be considerably more extensive than those of Britain. There are analyses of the coal of Tasmania, New South Wales, and Borneo, the Labuan kind (here by a typographical error given as Lahman), but there is no mention of the extent of the fields. There are likewise a number of analyses of New Zealand coal but with a similar omission. The same applies to the coal of India. This is unfortunate, since the coal-producing capabilities of the British empire naturally concern the reader more than those of the European Continent, or of the United States, concerning which there is a plethora of information. On the coal-fields of China we can find no data. Now, as the deposits in that empire are reported to exceed in extent even those of America, we hoped to find here trustworthy data. The coal of Saghalien, which has been seized by Russia on this very account, as well as that on the Amur and in Corea, have been found unfit for steam purposes. Hence it is possible that the Chinese coal may prove to be of similar quality.

On the luminosity of flame we find an interesting account of the most recent results. It is well known that Dr. Frankland called in question the old theory of the luminosity of flame, and ascribed it as, in many cases at least, due to the existence of a high temperature, and to the presence of gases and vapours of great density. This, however, according to the more recent investigations of Soret and Burch, is not invariably the case. The luminosity of a candle flame is, at all events, due to intensely ignited solid matter. It has been found that when the image of the sun was projected, by means of a lens, on the flame of a candle a spot of light appeared, and this light, when examined with the spectroscope, showed distinctly all the Frauenhofer lines. When examined by means of a Nicol's prism the light was found to be completely polarised at right angles to the line of incidence, proving that it was reflected from solid particles.

As regards liquid fuel we find no expression of opinion as to its origin. It is said that the Kimmeridge shales, of Dorsetshire, of which there is practically an unlimited supply, yield 40 gallons of crude oil per ton. So far, however, as we have come in contact with this product, we have found it of a most evil odour, whence we fear that its satisfactory purification would prove expensive.

The subject of natural gas receives full attention. At Pittsburg it has been found that 1000 cubic feet of gas was equivalent to $81\frac{33}{49}$ lbs. of coal. But the coal in question is worth only 5s. per ton, so that the fuel value of the natural gas, if it is to compete with coal, must not be above twopence per 1000 cubic feet. Hence, the expense of winning, piping, and managing, and gas-supply must be very low if it is to yield a profit upon this valuation. For metallurgical purposes it has the advantage of being free from sulphur.

The advantages, or disadvantages, for domestic lighting purposes of the so-called "water-gas" are not here discussed. But the analyses quoted show a very considerable variety in its composition, according to the process used. The dangerous ingredient, carbon monoxide, may reach 28, 31, or even 35 per cent.

Among other important questions here dealt with, but which space does not permit us to notice, are the more complete recovery of the nitrogen present in coal, the elimination of sulphur from coke, the recovery of the oily and tarry matters given off from coke-ovens, the remunerative treatment of peat, &c.

To competent men this book will carry with it its own urgent recommendation.

Watts' Manual of Chemistry, Theoretical and Practical (Based on Fownes' Manual). Vol I. Physical and Inorganic Chemistry. Second Edition (Fourteenth Edition of Fownes'). By W. A. Tilden, D.Sc., F.R.S., Professor of Chemistry in the Mason College, Birmingham. London: J. and A. Churchill.

"Fownes' Manual" has long, and with full reason, been a general favourite among teachers and students, as will be at once seen from the fact that the present is the fourteenth edition. In the successive hands of Watts and of Dr. Tilden it has undergone such additions, emendations, and general modifications as the rapid growth of chemical science demand, and we have full reason for asserting that in its present form it will be even more highly valued than its predecessors have been.

Among the principal alterations in this edition we note the suppression of the section on Physics. Much of the matter which it contained is incorporated with the text in appropriate parts of the work, and for fuller instruction the student is referred to special physical text-books, of which there is now no lack.

There has also been introduced, apparently in accordance with the original intention of Fownes, a series of systematic directions for an elementary course of experiments.

The recent results of research, wherever they can be regarded as definitely established, have been fairly brought forward. As instances of this the reader is referred to the sections on the Periodic Law, the Spectroscope as an Instrument of Chemical Investigation, and on the Rare Metals. Generally speaking, we are surprised at the quantity of information which has been condensed into this volume, and that without any sacrifice of clearness.

We are much pleased at the total absence of all reference to examinations. The editor's great object has been not that the student should "pass," but that he should know. We can only express our confidence that the work will be appreciated as it unquestionably deserves.

Outlines of the Clinical Chemistry of Urine. By C. A. MacMunn, M.A., M.D. (Dublin). London: J. and A. Churchill.

The object of this work is to present the chemistry of urine in health and in disease in a form calculated to suit the requirements of the medical practitioner.

The author sets out with an account of the function of the kidney and the mechanism of its secretion. In the second chapter we have an account of the general characters of normal human urine, followed in the next chapter by a description of the constituents of normal urine, and instructions for the estimation of urea by Liebig's process and by the hypobromite method. For the determination of total nitrogen Pflüger and Bohland's modification of the Kjeldahl process is recommended. The methods of J. A. Wanklyn for determining urea and nitrogen are not mentioned.

In the succeeding chapters we find descriptions of uric acid and allied bodies, such as allantoin, creatinin, xanthin, &c., the non-nitrogenous organic acids, the aromatic bodies, and colouring matters of urine. Here the author describes a pigment giving a very characteristic absorption-spectrum, and which he has named "urohæmatoporphyrine."

Among the inorganic constituents of urine hydrogen peroxide is mentioned, on the authority of Schœnbein. There is also a notice of a condition known as phosphaturia, on the recognition of which Dr. MacMunn lays more weight, as it is misinterpreted by quacks to the great alarm of their unhappy patients.

The second part of the work treats of the abnormal constituents of urine, serum, albumen, and other proteids, blood and bile, sugars, acetone, and diacetic acid, fatty bodies, crystine, tyrosine, leuceine, and oxymandel acid.

The concluding part of the work is devoted to urinary deposits and calculi and the detection of various drugs or poisons in urine.

The instructions for the determination and estimation of the constituents of urine, normal or abnormal, are fully on a level with the science of the day, and will render this work a valuable book of reference for the faculty. We are pleased to find here a chart of the absorption-spectra with the necessary explanations.

Service Chemistry; Being a short Manual of Chemistry and its Applications in the Naval and Military Services. By Vivian B. Lewes, F.I.C., F.C.S., Professor of Chemistry, Royal Naval College, Greenwich. London: Whittingham and Co.

This work is a new departure. Chemistry has, of course, weighty words to say in military and naval affairs, as, indeed, in almost every department of human activity. But, in the English language at least, no systematic attempt has been made to call attention to such lessons.

The author, rightly enough, says that there is but one chemistry, and that its technical adaptation to any special subject is merely an amplification of the science in one particular direction. Still, it strikes us that the officers and others, for whose use this work has been specially arranged, might have been more advantageously referred for general principles to some one of the many chemical manuals now in existence.

The subjects principally noticed are fuel, explosives, drinking-water, boiler incrustations, corrosion and fouling of iron ships, paints, ventilation, &c. The instructions given concerning drinking-water seem to us scarcely sufficient; nothing is said concerning the analysis of waters with a view to the detection of doubtful or injurious ingredients, organic or inorganic. Now, such information must be very necessary for troops on the march, or during a campaign. For want of better knowledge, too, the captain of a ship may fill his tanks with bad water.

Directions for Clarkising and filtering impure water are given very carefully and at some length. The comparative effects of animal charcoal and of "carbalite" upon Thames water have been tested in a series of special experiments. It appears that the charcoal was rather the more effective in removing "total solids" and chlorine, but that carbalite had the advantage as far as "free" and "albumenoid ammonia" are concerned. These experiments might have been usefully extended so as to include Anderson's scrap-iron filter, Bischof's spongy iron, and Doulton's manganous carbon. The author makes an indirect mention of the value of alum in precipitating organic matter held in solution in impure waters; saying that it is one of the ingredients of Maignen's "anti-calcaire," but the Chinese have used alum for this purpose for thousands of years. This process is much to be recommended under circumstances where filters of any size cannot be conveyed. It is merely necessary to put the water in a tub, add a few grains of alum, stir up, and let settle. The clear liquid above may then be drawn off and used with safety, whilst the water without such treatment would prove highly dangerous. It must not be supposed that the absence of animal pollution proves that a water is safe. In some very scantily peopled districts the water of the springs may be very seriously polluted, as some savage tribes, both in Africa and America, have the abominable custom of burying their dead beneath springs and shallow streams.

The behaviour of different kinds of water when used for raising steam receives due notice. In this connection the author points out that if animal or vegetable oils—any other than mineral—are used for lubrication they are split up by the superheated steam, and the fatty acids being set free, corrode the boiler plates.

As regards the prevention of incrustation the author

thinks that in the case of marine engines no agent added in the boilers gives satisfactory results. The water should undergo a suitable treatment before being pumped into the boilers. For land engines, where only hard water is to be procured, he prefers sodium carbonate or paraffin oil. Animal and vegetable oils and fats he very justly condemns altogether.

In connection with the production of saltpetre we find mention of a curious fact observed by the late Professor Bloxam, viz., that "the urine of a man would furnish 2 ozs. of saltpetre daily, an amount sufficient to make nine rounds of small-arm ammunition."

Mr. Lewes is to be congratulated on the general idea of this book, as he will easily be able to eliminate its defects in future editions.

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

SIR,—In the CHEMICAL NEWS (vol. lx., p. 208) "The Writer of the Report" (which appeared in vol. lx., p. 157) asks me, in the interests of science, to give the composition and properties of my reagent, and to explain the *rationale* of its formation. To this invitation I shall gladly respond as soon as certain investigations now in progress are completed.

What the writer of the report calls a very serious mistake in my "Notes Relating to the Demonstration at Wimbledon," only appears so to him in consequence of misapprehension. I do not for one moment dispute that other sludges may be inoffensive, even when first drawn from the tank; but does the writer of the report know of any which would, like that from the "Amines" process, keep inoffensive if tipped on to land without further treatment, and exposed during the summer months to alternating sunshine and showers? Since this involves my chief claim, namely, sterilisation, in other words, complete and permanent disinfection, would it be too much to ask the writer to name the process, or processes, to which he alluded?—I am, &c.,

HUGO WOLLHEIM, Managing Director.

The "Amines" Syndicate, Limited,
101, Leadenhall Street, London, E.C.
October 29, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 15, October 7, 1889.

New Observations on the Reciprocal Displacements between Oxygen and the Halogens.—M. Berthelot.—This paper will be inserted in full.

Facts towards the History of Raffinose.—M. Berthelot.—Raffinose presents itself in two different forms according to the conditions of its crystallisation. When it is caused to crystallise from alcohol it is generally obtained in small hard granulated crystals containing 15·1 per cent water of crystallisation. This is the ordinary form described by Loiseau, Scheibler, Ritthausen, and Tollens. It answers to the formula $C_{36}H_{32}O_{32} + 5H_2O_2$. The author has also obtained it in another form from aqueous alcohol containing from 17 to 18 per cent of water, and agreeing with the formula $C_{36}H_{32}O_{32}+6H_2O_2$. Possibly there exists also a third hydrate containing $4H_2O_2$.

Synthesis of Certain Oxygenated Selenium Compounds belonging to the Aromatic Series.—C. Chabrié.—The author first tried to oxidise phenyl selenide directly by nitric acid, potassium permanganate, and chromic acid. With nitric acid he obtained nitro-products; with the two others no definite compounds were produced. On treatment with oxygenated water mixed with hydrochloric acid he obtained a body containing oxygen, but this element was fixed upon the phenylic nucleus and not combined with the selenium. Lastly, he caused the dichlorhydrine of selenious acid to react upon benzene in presence of aluminium chloride. According to the proportions he obtained diphenyl-selenine or its chlorine derivative.

Researches on Fucusol.—M. Maquenne.—The author shows that the fucusol of Stenhouse is a mixture of furfurol and methyl-furfurol in the proportion of ten parts of the first to one part of the second. The name of *fucusol* not applying to any definite proximate principle should therefore be abandoned. The molecular structure of methyl-furfurol has still to be determined.

On the Presence of Pectic Compounds in Plants.—Louis Mangin.—The author shows the presence of pectic compounds in vegetable membranes, where they are constantiy present, and more rarely in the cellular cavity, as in the leaves of yew, of *Calla æthiopica*, and in the flowers of the hyacinth.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iii., July, 1889.

New Theory of the Double Elliptical Refraction of Quartz.—Dr. G. Quesneville.—This paper is not adapted for useful abstraction.

The Methods and Procedures for producing Chlorine and Hydrochloric Acid by Means of Magnesium Chloride.—Dr. G. Eschelmann.—The author describes and criticises the processes of Schlœsing and of Weldon-Pechiney. He considers that the latter merits most attention, and expects that it will confer upon Stassfurt a monopoly of the manufacture of chlorine-products for the entire world.

The True Formula of the Permanganates.—Ch. Bradbury.—From the CHEMICAL NEWS.

Recent Synthetic Experiments in the Series of the Saccharine Matters.—E. H. Keiser.—From the *American Chemical Journal.*

Scientific and Industrial History of Aniline Black.—Prof. E. Noelting.—Already noticed.

Lecture Experiments on Nitric Acid.—P. Austen.—From the CHEMICAL NEWS.

The Use of Hydrogen Peroxide in Analysis.—Mr. Dunnington.—From the CHEMICAL NEWS.

The Great Chemical Industries at the Paris Exhibition.—P. Kienlen.—A list of exhibitors with brief notices of the articles displayed.

Green Ultramarine.—Dr. Szilazi.—From *Liebig's Annalen.*

On the New Metal, X, Extracted from Cobalt and Nickel.—Prof. G. Krüss and F. W. Schmidt.—Already noticed.

Industrial Society of Mulhouse.—Session of May 8, 1889.—M. Albert Scheurer sent in a paper on thioflavine, a new yellow basic colouring-matter manufactured by Casella and Co., of Frankfurt. It is soluble in water and in alcohol, very soluble in acetone, acetine, and acetic acid. It is readily fixed by means of tannin. The following colour gives good results on cottons:—40 parts thioflavine, 50 tannin, 50 water, 100 acetic acid, 60 acetine, and 700 gum water. Steam and pass through tartar.

emetic. It is nearly as bright as chrome yellow, resists light, and does not soil the whites.

Extraordinary Session, May 22, 1889.

The session was devoted to a revision of the list of prizes. H. Kœchin sent in a sample of an artificial textile fibre, dyed in rhodomie, more brilliant and beautiful than silk. The fibre is prepared at Lyon by a patented process from a solution of gun-cotton. It is much weaker than silk.

A New Series of Aluminium Compounds.—Already noticed.

Ferro-Manganese with a Low Percentage of Carbon.—Sergius Kern.—From the CHEMICAL NEWS.

MISCELLANEOUS.

University College Chemical and Physical Society.—On Wednesday, November 6, at 4.30 p.m., a paper will be read on "The Nature of Electricity," by A. H. Fison. D.Sc.

Appointment.—Mr. D.S. Macnair, Ph.D., F.C.S., &c., has been appointed by the Trustees Instructor of Chemistry in the People's Palace Technical Schools, London. Dr. Macnair, who has proved himself to be an excellent teacher, and also capable of carrying on original research, was very highly recommended by Sir Henry Roscoe, and by Professor Emil Fischer, of Würzburg.

Physical Society of Liverpool.—It is proposed to form a Physical Society in Liverpool, which will hold its Meetings at University College, and Professor Oliver Lodge has consented to be nominated as first President. The Preliminary Meeting will be held in the Physics Theatre of the University College, at eight o'clock, on Wednesday evening, November 6th, Professor Oliver Lodge in the chair. Local students and all others interested in the subject are invited to be present. The Secretary (pro tem.) is Mr. Thomas Tarleton, 1, Hyde Road, Waterloo, Liverpool.

MEETINGS FOR THE WEEK.

MONDAY, Nov. 4th.—Society of Chemical Industry. "An Account of a Borax Lake in California," by C. Napier Hake.

—— Royal Institution, 5. General Monthly Meeting.

THURSDAY, 7th.—Chemical 8. "The Isolation of a New Hydrate of Sulphuric Acid existing in Solution," by S. U. Pickering. "Further Observations on the Magnetic Rotation of Nitric Acid of Hydrogen Chloride, Bromide, and Iodide in Solution," by Dr. W. H. Perkin, F.R.S. "On Phosphoryl Trifluoride," by T. E. Thorpe, F.R.S., and F. T. Hambly. "On the Acetylation of Cellulose," by C. F. Cross and E. Bevan. "On the Action of Light on Moist Oxygen," by A. Richardson. Anhydracetophenonebenzil and the Constitution of Linius Lepidens," by Drs. Japp, F.R.S., and Klingeman.

TO CORRESPONDENTS.

M. T. S.—The question is on "Avogadro's Law." See Kolbe's "Inorganic Chemistry," by Humpidge (Longman's), pp. 50, 575.

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See opinion *Electrical Review*, October 21.

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THE CHEMICAL NEWS.

Vol. LX. No. 1563.

RE-EXAMINATION OF THE SPECTRA OF TWENTY-THREE GAS-VACUUM END-ON TUBES, AFTER SIX TO TEN YEARS OF EXISTENCE AND USE.*

By C. PIAZZI SMYTH, late Astronomer Royal for Scotland.

When looking over lately, in the spectroscope, a number of end-on gas-vacuum tubes, of ages between six and eleven years, and by diverse makers in Paris, London, and Edinburgh, the too usual impurity of hydrogen lines was found abundantly in almost all of them; while even still more noticeably there were seldom any two where the relative intensities of the principal lines of both high and low temperature hydrogen ranged exactly together through a large part of the spectrum.

But intensity of light, whether relative or absolute, so long as it keeps within moderate limits, is of very small importance in spectroscopic research; while, on the other hand, the question of the absolute spectral place of a line, or the spectral distance of one line from another, is a fact of most crucial value, no matter to what excessively small extent any change therein may be established under particular circumstances. In cases, then, where the intensity of the lines has changed *much*, may their spectral places have changed a *little*; and if the general belief is to the contrary, has that impression been arrived at by theory, or from the result of careful micrometrical measures? And, either in one way or the other, has it been positively proved that hydrogen gas may not sometimes be modified in its spectral action, when shut up in an attenuated state, in a glass tube with a larger amount of some other gas for several years, and provoked through the greater part of that time by electric sparking to form some possible combination with its neighbour?

Enquiry by practical experiment seemed to me, with measuring apparatus in hand, the best answer to attempt, though it was not very hopeful, as my dispersion power available at the time was not great. But the case seemed at least worth trying, if only to be thereby authoritatively laid on the shelf again, and the spectroscope set free for other work.

Starting then with four tubes prepared in three countries positively for pure hydrogen and nothing else, three of their high and one of their low temperature lines, forming together a well-stepped and fiducial series between red at one end and violet at the other, were chosen and micrometrically measured again and again in spectrum place, both direct and reversed, as well in the tube's position before the slit as in direction of current, but without alighting on any anomaly. In fact every one of these tubes of intended hydrogen gave exactly the same spectrum of place for its lines as every other; so that each formed an invaluable scale of place-reference for the lines of any unknown or suspected incandescent gas.

Next were examined in the same apparatus—

Two	tubes	of carbonic oxide	with	hydrogen	therein.
One	,,	chlorine	,,	,,	,,
One	,,	cyanogen	,,	,,	,,
One	,,	hydrochoric acid	,,	,,	,,
One	,,	iodine	,,	,,	,,
One	,,	nitrogen	,,	,,	,,
One	,,	nitrous oxide	,,	,,	,,
Two	,,	olefiant gas	,,	,,	,,
Three	,,	oxygen	,,	,,	,,
Two	,,	mercury	,,	,,	,,

* Read before the British Association, Section A, Newcastle Meeting.

Although in all these tubes hydrogen lines were found in various intensities, yet all the closest measures, and in all the opposite positions possible for the tubes, failed to bring out any alteration of spectroscopic distance apart, as between any of the test lines shown by the smallest quantity of adventitious hydrogen in another gas's tube, and the same lines in any of the previous tubes of nothing but hydrogen. So that the electric spark would seem, where hydrogen is concerned, rather to preserve its purity than to promote its combination with something else present at the time; the sparks being confined to 1·5 inches in length, but the pressures at which the gases were included under hermetic seal varying from 0·05 to 0·50, 1·00, 2·50, and in one case even 4·00 inches of the barometer.

Other circumstances, however, that were not being looked for supervened, and fully repaid all the trouble spent as above in proving a negative, so far as such could be proved with a dispersion power of only 6·23°, and a magnifying power of no more than 15, but with exquisite definition.

These other circumstances were chiefly the progress of change in certain of the tubes subsequent to 1880, of one of which it was said and printed in 1880 that "it still shows its chlorine lines, but they are becoming fainter; while carbon bands and hydrogen lines have appeared, making its spectrum look very like what that of hydrochloric acid was at first." This chlorine-intended tube then, still testifying at that time for chlorine, has now, in 1889, nothing but hydrogen lines to show, and so brightly as to raise the question whether the chlorine can have changed into hydrogen within the walls of hermetically sealed glass.

Towards this end, however, we may derive some furthur and more unexpected information from a certain iodine tube of 1878: of which tube it was printed in the *Transactions of the Royal Society* (*Edinburgh*), 1880, that, "it heats unduly beneath the spark, as if inclined for a change, and has much deposited haze in the interior. But no perceptible alteration of spectrum has yet been noted; and because, perhaps, the maker, M. Salleron, in Paris, put so large a quantity of solid iodine inside, that there is no chance of its all being dissociated, or converted into something else by weak sparks, only one inch long, within any moderate time—if iodine is really, as some persons are beginning to suspect, not the elementary body which chemists have long believed, but a compound."

Now at that date, 1880, that iodine tube was showing no less than 148 iodine lines by measure between red and violet. Of those lines, necessarily of low electric temperature, no less than 50 were identified with the high temperature spectra of the greater observers of iodine, and included all its strongest lines, twelve of them being exceedingly strong and brilliant. And it was further written at that time that this tube's spectrum is most peculiar for its freedom from nearly all known impurities of other gases—*save* three exceedingly faint reproductions of the three chief hydrogen lines. Yet in the present year, 1889, there is not one iodine line left in that tube, and its spectrum range is filled with nothing but both low and high temperature hydrogen lines of astonishing brilliancy. While of the large amount of iodine granules hermetically sealed into the tube in 1878—only a very small amount of apparently inert dust is now left.

Whether this change is an infinitesimally small part of the progress of everything to turn into hydrogen, and for assisting thereby the whole solar system to explode some day into a so-called and spectroscopically bright-lined hydrogen star—I will by no means weary the Section by enquiring now. But if three minutes more can be allowed, I would beg leave to mention shortly something else that has also turned up in course of this investigation, and is of quite a comfortable character; viz., that the best of all the gas-vacuum tubes that have passed through my hands were made for me in London, and can, I suppose, be re-

peated there for all who choose to order them in an intelligent manner.

How much this means may be judged of by the fact that I was actually written to in wrathful terms by a South-Australian, whom I did not know, several years ago, because, forsooth, he, having on his own choice written to *some one* in London for examples of my "end-on" gas-vacuum, tubes received in due course a set of which he could make no use, by reason of their containing a medley of all or any gases. Wherefore he denounced London tradesmen generally, and declared that South Australia would soon be obliged to get on without them.

Now, however, I can inform all and sundry that out of eight tubes made for me by Mr. Charles Casella, the skilful son of the well-known Mr. Louis P. Casella, of Holborn, no less than five of them (viz., one of CO, two of N, and two of O) have stood the difficult test of being found, after six years' existence, in perfect freedom from any of that most insinuating of all gaseous impurities, hydrogen, and capable, therefore, of being studied for the lines of their intended gases under unusually favourable circumstances.

Clova, Ripon, July 25, 1889.

REPORT OF THE COMMITTEE ON INDEXING CHEMICAL LITERATURE.*

The Committee on Indexing Chemical Literature respectfully presents to the Chemical Section its seventh annual report.

During the year just closed three bibliographies have been published by the Smithsonian Institution.

A Table of Specific Gravity for Solids and Liquids. The Constants of Nature, Part I. (new edition, revised and enlarged). By Frank Wigglesworth Clarke. Washington, D.C., 1888. Smithsonian Miscellaneous Collections, No. 659. 8vo., pp. xi., 409.

This volume contains the specific gravities of 5227 distinct substances and 14,465 separate determinations, being more than twice as many as in the first edition with supplement.

Index to the Literature of Columbium, 1801-1887. By Frank W. Traphagen. Smithsonian Miscellaneous Collections No. 663. Washington, 1888. 8vo., pp. [iv.], 27.

This Index contains the threefold arrangement chronological, alphabetical by authors, and subject-matter. The abbreviations of Journal-titles are those adopted by the Committee on Indexing Chemical Literature, upon whose recommendation this index was printed.

A Bibliography of Chemistry for the Year 1887, by H. Carrington Bolton. Washington, 1888. Smithsonian Miscellaneous Collections No. 665. 8vo., p. 13.

Prof. Wm. L. Dudley, Vice-President of the Chemical Section of the A. A. A. S., has appended to his address on the Nature of Amalgams an Index to the Literature of the subject, which will be printed in the forthcoming volume of the *Proceedings* of the Toronto meeting.

We record the publication of the following index. Lists of patents relating to Soap and Candles in "Manufacture of Soap and Candles," by Wm. Brannt, Philadelphia, 1889.

Also:—An Index of Researches upon the Production of Ammonia from Atmospheric Nitrogen. By Ezra J. Ware. Published in *Proceedings Michigan State Pharmaceutical Association*, 1888; H. J. Brown, Ann Arbor, Mich., Secretary.

Reports of progress from several volunteer indexers have been received. Dr. Alfred Tuckermann has completed his Index to the Literature of Thermo-dynamics, except a subject-index to which he is putting finishing touches. He has also begun an Index to the Literature of the Chemical Action of Light, a subject suggested by the Chairman of your Committee.

The publication of this annual report is always followed by numerous applications for information, especially with respect to the method of indexing adopted by the Committee. These inquiries we may in some degree anticipate by repeating the statement that this Committee does not prescribe any standard nor dictate any system for volunteers to follow. Those interested in the work of the Committee would do well to examine the six reports already published, in which will be found suggestions for systematic indexing (1885), a complete list of indexes already printed under the auspices of the Committee (1887), and a list of "Abbreviations of Titles of Chemical Journals," intended to secure uniformity in references (1887).

The choice of subjects for indexing has generally been made by the volunteers themselves; in a few instances only the topics have been suggested by the committee, at the request of co-workers. These subjects, as shown in our reports, cover a wide range in physical, inorganic, and organic chemistry; the desirability of procuring indexes to individual elementary substances should not be overlooked by those who contemplate offering aid. A few copies of the Report of 1887 (which includes lists as above) remain, and can be had on application to the chairman, to whom, also, letters of inquiry may be addressed, care of Smithsonian Institution, Washington.

H. Carrington Bolton, *Chairman.*
F. W. Clarke.
A. R. Leeds (in Europe).
A. A. Julien,
John W. Langley.
Albert B. Prescott.
Chas. K. Wead.

* Advance proof from the *Proceedings of the American Association for the Advancement of Science*, vol. xxxviii.

THE PRESENT METHODS OF TEACHING CHEMISTRY.*

(Concluded from p. 219).

IX. *Recommendations of the Elementary Education Commission Report* (1888) *affecting Chemical Teaching.*

The recommendations in the recent report of the Elementary Education Commission are very favourable to science-teaching, as may be seen from the following extract:—

"If it be true, as we believe it is, that the object of elementary instruction is to give such instruction to the scholars in general as will best fit them to fulfil the ordinary duties of life to which they are most likely to be called, and to enable those who may be endowed with special gifts to rise to still higher callings, then elementary instruction in science—and we lay special stress upon the word "elementary"—is only second in importance to elementary instruction in reading, writing, and arithmetic. But the fact has impressed itself upon our minds that technical training does not exist for boys even to the extent that instruction in needlework and cookery supplies it for girls. We have had, however, a great deal of evidence showing the educative effect of science-teaching in elementary schools for both boys and girls; and we think that science, especially mathematical, mechanical, and physical science, is not only the foundation, but an essential part of thorough technical instruction.

* Report of the Committee appointed for the purpose of inquiring into and reporting upon the Present Methods of Teaching Chemistry (consisting of Professor H. E. Armstrong, Professor W. R. Dunstan (Secretary), Dr. J. H. Gladstone, Mr. A. G. Vernon Harcourt, Professor H. M'Leod, Professor Meldola, Mr. Pattison Muir, Sir Henry E. Roscoe, Dr. W. J. Russell (Chairman), Mr. W. A. Shenstone, Professor Smithells, and Mr. Stallard). Read before the British Association, Section B, Newcastle Meeting.

"There are, however, certain broad principles to be laid down as necessary conditions of introducing science-teaching into elementary schools. In the first place care must be taken that it is not introduced too early in school life, lest it should interfere with the scholars' general instruction. In the second place we are of opinion that, as a rule, the ordinary elementary master cannot be expected to be a good science master. Even in the case of an elementary teacher who, while at the training college, has made good progress in science studies, we consider that he has so much also to do in the usual school routine, and that his attention is so much distracted from science, that he cannot be relied on either for clear, vivid, and simple lectures, or for neatness and certainty in the performance of experiments. But to possess the power successfully to achieve these results is an essential qualification in a science teacher, and especially so in one who has to expound experimental science to the class who attend our elementary schools."

In addition to general recommendations in the sense of the above quotation, the chief are—

(*a*). That object lessons should be continued in the lower standards in succession to similar teaching in the infant schools.

(*b*). That the system of peripatetic demonstrators should be encouraged.

(*c*). That more attention should be given to the possession of an adequate knowledge of natural science in the appointment of H.M. inspectors.

(*d*). That examinations in science should as far as possible be conducted orally, and not on paper, especially in the first five standards.

(*e*). That higher grades of elementary schools should be recognised as continuation schools.

(*f*). That technical instruction should be placed in the hands of, and mainly supported by, "local authorities," and be controlled by the Education Department.

(*g*). That the evening school system should be thoroughly revised so as to admit of (1) special curricula suitable to the locality; (2) attendance on "additional subjects" without at the same time taking the three R's; (3) attendance of scholars over twenty-one years of age. Also that a greater fixed grant should be awarded, and less be made to depend on individual examination.

X. *The New Proposal Code* (1889) *and Chemical Teaching.**

The chief changes contemplated in the new code are as follows:—

(*a*). The grant on results of examination in the three R's is cancelled, and the merit-grant disappears as a separate grant. The grants for elementary science and chemistry as a specific subject are, however, unaltered, *i.e.*, they are still based on results of individual examination.

(*b*). English is no longer compulsorily the first-class subject, and the position of elementary science is thus improved.

(*c*). Scholars of any public elementary school may attend science classes at any place approved by the inspector, and still earn Government-grants.

(*d*). Day-training colleges are recognised. Teachers of chemistry may thus be trained in the existing university colleges with a Government capitation grant of £35 per annum. The precise conditions are not yet defined. A third year of training is recognised for the first time.

(*e*). The conditions of age and grants are retained in evening schools, but a scholar who has passed Standard V. may be examined in "additional" subjects—*e.g.*, chemistry without the three R's.

These alterations, together with other minor ones, give greater freedom to the teaching in elementary schools, and especially influence the teaching of chemistry (1) by releasing the pressure due to the necessary individual "passing" in the three R's; (2) by making it possible for elementary science to be the first optional subject taken; (3) by allowing scholars to go outside for science instruction; (4) by making the chemistry-teaching in university colleges available for the training of teachers.

The code, however, as will be seen, falls short of the recommendations of the Elementary Education Commission so far as science teaching is concerned.

Postscript to Appendix.

The Technical Instruction Act (1889) *and Chemical Teaching.*

The Government Bill introduced and passed at the end of the recent session differs from Sir Henry Roscoe's Bill, referred to in the Appendix VIII., *ante*, in several respects. It provides mainly that the "local authority" (county or borough council, or urban sanitary authority) shall have power to contribute money to all schools and institutions not conducted for private profit in aid of all the sciences and arts relating to industries, and also in aid of manual instruction. The money is to be raised by a local rate not exceeding one penny in the pound in one year. The range of subjects of study and the relative aiding of different schools is to be regulated by the Science and Art Department. The effect of the Act will not be felt in the truly elementary schools, but it will greatly encourage the teaching of chemistry and other sciences to children who have passed the Standards.

From those who are engaged or interested in the teaching of physical science the Committee will be glad to receive any information which is likely to be of service in showing how their suggestions may best be carried into effect. It is requested that these communications be addressed to Professor Dunstan, 17, Bloomsbury Square, London.

THE MANUFACTURE OF THE ALLOYS OF ALUMINIUM IN THE ELECTRIC FURNACE.*

By JOHN H. J. DAGGER, F.I.C., F.C.S.

(Continued fom p. 213).

I have now described the most important features of the electro-metallurgical industry as carried on at Milton, and will proceed to describe the chief properties of the alloys produced and some results obtained from them.

With copper, aluminium forms a series of interesting and beautiful alloys, varying in colour from bluish white to red gold and pale yellow, and also differing widely in physical and mechanical properties.

Alloys containing 60 to 70 per cent aluminium are very brittle, glass-hard, and beautifully crystalline; with 50 per cent the alloy is quite soft, but under 30 per cent the hardness returns. The 20 per cent bronze has a whitish yellow tint, and somewhat resembles bismuth; it is very brittle, and can be pulverised in a mortar.

The brittleness of alloys containing more than 11 per cent prevents their use, but from 11 per cent down to 1¼ they are of very great value, possessing great tensile strength, high resistance to compression, low specific

* See article by Dr. Gladstone, "The New Code and Science-teaching," *Nature*, May 2, 1889; also statement issued by the National Association for the Promotion of Technical Education, "The New Education Code," 1889.

* Read before the British Association, Section B, Newcastle Meeting.

gravity, and greater resistance to corrosion than any alloy known.

The following gives the density of these alloys compared with other metals and alloys.

Metal.	Density.
Aluminium bronze 3 per cent	8·69
,, ,, 4 ,, ...	8·62
,, ,, 5 ,, ...	8·37
,, ,, 7·5 ,, ...	8·00
,, ,, 10 ,, ...	7·69
,, ,, 11 ,, ...	7·23
Brass	8·38
Cannon bronze	8·23
Cast ,, ...	7·20
Cast steel	7·71
Iron	7·80
Nickel	8·57
Silicon	2·67
Platinum	21·50
Gold	19·30
Lead	11·40
Silver	10·50
Copper	8·90
Tin	7·50
Zinc	7·10

The standard "A" grade, containing 10 per cent aluminium, behaves as a true alloy—that is, will not liquate out into different combinations. It resembles pale gold in colour; its tensile strength in castings runs from 75,000 lbs. to 90,000 lbs. to the square inch, with from 4 to 14 per cent elongation.

The following is the report of a test of 10 per cent bronze produced by the Cowles process, made by Prof. Unwin, and alluded to in his work on the "Testing of Materials of Construction," p. 348.

The bar was 0·499 in diameter, and was placed in shackles which have spherical bearing surfaces, so that the tension was extremely uniform on the section:—

Breaking weight 7·195 tons = 36·78 tons per sq. inch 86·743 lbs.

Elongation in 10 inches 3·326 inches = 33·26 per cent.

Contraction of area 0·078 inch = 39·87 per cent.

Elastic limit 3·47 tons = 17·74 tons per sq. inch.

The elongation in different parts of the bar was much more uniform than with iron or steel.

One-inch lengths measured after fracture:—

No. 1.	2.	.	4.	5.	6.
1·27	1·27	1·26	1·28	1·27	1·26
7.		**9.**	**10.**	**11.**	**12.**
1·28	1·29	1·34	1·36	1·44	1·44

Test at Washington Navy Yard of Cowles Co. "Special Grade" Aluminium Bronze.

Specimen. No.	Dimension of specimen. Length in inches.	Diameter in inches.	Weight applied in lbs.	Elastic limit per sq. inch on original cross section. Lbs.	Weight per sq. inch on original cross section. Lbs.	Elongation per cent.	Reduction of area per cent.
1.*	2·00	0·500	22,485	—	114,514	0·45	0·00
3.	2·00	0·501	21,650	79,894	109,823	0·05	39

Ordnance Office, Navy Yard,
Washington, February 16th, 1886.

A. H. McCormick,
Commander, U.S.N., Inspector of Ordnance.

* Cu 89·0, Al 10·0, Si 1·0=100.

The high elastic limit in a material so plastic is noteworthy. In *resistance to compression* this metal equals the best cast steel; its *transverse strength*, or rigidity, is about forty times greater than ordinary brass; its limit of elasticity equals steel of the same tensile strength and elongation. Forged, tempered, and annealed, its elongation equals the best grades of steel of the same strength.

The "special" grade contains more aluminium than "A" grade; is higher in tensile, transverse, torsional strength, and elastic limit. Its elongation is less, ranging from nil to 8 per cent.

Accompanying was a test made at Washington Navy Yard, of metal of this grade, supplied by the Cowles Co.'s works (see preceding column).

Test Made in Leeds, England.

The Leeds Forge Co., Lim.,
Testing Department.

"Special Grade" Aluminium Bronze.

Nov. 10th, 1886.

Specimen.	Dimensions in inches. Diam.	Area.	Tensile strength in tons. Total per sq. inch.
1 round bar casting ..	0·285	0·0646	57·27 (128,400 lbs.)

For the Leeds Forge Co.,
(Signed) Sampson Fox, May, & Co.

The B, C, D, and E grades, containing 7½, 5, 2½, and 1¼ per cent aluminium respectively, decrease in tensile strength from about 65,000 per sq. inch in B to 25,000 lbs. in E grade. The transverse and torsional strength, elastic limit, and resistance to compression decreasing as the aluminium is lowered; elongation increasing in the same proportion. The E grade metal will stretch nearly two-thirds of its length before rupture, which exceeds that of pure copper by about 100 per cent. A piece of C grade wire can be twisted through several hundred turns before breaking. A rolled bar of C grade (5 per cent), tested at the Phœnix Works, Rohort, Germany, gave—

Tensile strength .. .. 82,880 lbs. to sq. inch—37 tons.
Elongation .. .. .. 60 per cent.

Average strength in castings:—

Grade.	Tensile strength per sq. inch.	Elongation.
"A" special (11 p.c.) ..	90—100,000	0—8·0 p.c.
"A" bronze (10 ,,) ..	75—90,000	4—14 ,,
"B" ,, (7½ ,,) ..	55—65,000	20—40 ,,
"C" ,, (5-5½ ,,) ..	35—45,000	30—40 ,,
"D" ,, (2½ ,,) ..	30—35,000	40—50 ,,
"E" ,, (1¼ ,,) ..	25—30,000	40—55 ,,

All grades of this bronze under 11 per cent can be rolled, swedged, or drawn cold, and is the only bronze that is not "hot-short," and can be worked at a bright red heat as easily as wrought-iron. Under the hammer it can be drawn out to the fineness of a needle.

The rolling of sheets, rods, bars, and wire is done at bright heat, only the finishing done cold. Rolling or working this metal in any way makes it stronger and tougher. A "rolled" rod, "B" grade, tested at the Otis Iron and Steel Works, Cleveland, Ohio, showed tensile strength 83,000 lbs. to the sq. inch, with 39 per cent elongation before breaking. In the casting this metal had but 60—65,000 lbs. tensile strength with 20 per cent elongation.

The fracture of the special and "A" grades exhibit a crystalline structure; the lower grades are extremely fibrous.

The beautiful colour and power of resisting corrosive influences make aluminium bronze valuable in art metal work.

In the church of St. Germain, Paris, are twelve beautiful candlesticks, six feet high, and a crucifix four to five

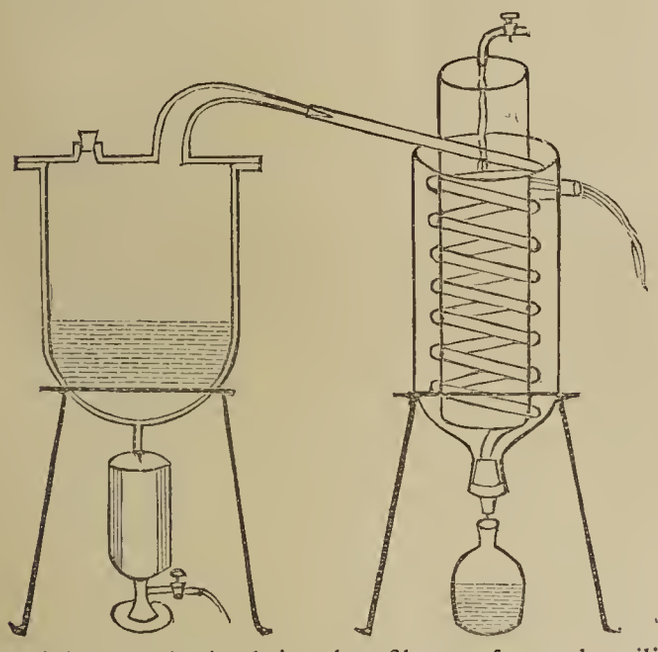
feet in height, made of 5 per cent aluminium bronze—these have been in position over twenty years, and their colour is still perfect. In Philadelphia the statue of Wm. Penn, intended to surmount the dome of the new city hall, will be cast in aluminium bronze.

(To be continued).

ESTIMATION OF SILICA AND ANALYSIS OF SILICEOUS MATERIALS.

By GEORGE CRAIG.

The process in most general use for estimating silica is, I believe, to fuse with alkaline carbonates and decompose with HCl, with subsequent evaporation to dryness. From many experiments it seems that no more than 97·5 per cent of the total silica can be obtained when pure silica or siliceous matter is subjected to the treatment just mentioned. The subsequent estimation of the silica remaining in solutions is a very tedious operation, and unsatisfactory after all. By decomposing with H_2SO_4 this difficulty may be overcome, and all the silica obtained insoluble; but the large amount of alkaline salts, introduced for purposes of fusion, necessitates the re-solution and re-precipitation of the Al_2O_3, MnO_2, CaO, and MgO



precipitates obtained in the filtrate from the silica. Thereby ammonia and soda salts increase to such an extent that their solvent action on the precipitates and on the operation-vessels becomes considerable. So much is this the case that, by evaporating the filtrate from the MgO precipitate to dryness in a platinum basin, expelling all volatile salts, dissolving in water, and rendering alkaline with Na_2CO_3, a considerable precipitate is obtained, consisting of SiO_2, Al_2O_3, CaO, MgO, and P_2O_5. The unreliability of figures obtained under such circumstances caused me long ago to discard the fusion process, and in all cases to expel SiO_2 with HF and H_2SO_4, and estimate the other ingredients in the residue. As may be imagined, careful analyses of the same material by both processes, using glass and porcelain vessels, show considerable differences, and there can be no doubt which is the more correct. I have no doubt this process is used by a great number of chemists; but the publication, ever and anon, of analyses performed by fusion processes convinces me that the errors inherent to the one and the accuracy and rapidity of the other are not sufficiently known—hence this communication.

For the expulsion of the silica, sufficiently pure H_2SO_4 may be had from the dealers, which is best employed after dilution with an equal vol. of water.

Commercial HF requires to be re-distilled, and for this purpose is introduced into a 10 or 12 ozs. capacity leaden retort and the vapours passed through a coil of red india-rubber tubing (¼ in. bore) immersed in water. The tubing is best wound spirally about a piece of 2 in. diameter glass tube, which serves to support it, and, at the same time, to introduce the cold feed-water at the bottom of the containing vessel, which is the same as that supplied with the ordinary spiral glass condensers. The arrangement is shown in the accompanying sketch. The first portion of the HF distilled is rejected, or it may be re-distilled, as it is contaminated with impurities derived from the rubber, but after a little the distillate leaves no residue on evaporation.

A blank experiment should be performed by evaporating 100 grains of the H_2SO_4 to dryness with a little HF, and ascertaining the weight and nature of the ignited residue, so that it may be allowed for.

Process.—20 or 25 grains of the very finely ground material are placed in a deep platinum crucible and H_2SO_4 added in quantity more than sufficient to form sulphates with all the bases present. About 50 grains bulk of the pure HF is added, and, after mixing well by shaking gently, the crucible is kept over the lowest flame of an Argand until almost dry. One treatment with HF is usually sufficient to expel all the SiO_2, but for surety I always repeat the operation, and heat more strongly at the finish *until H_2SO_4 is evolved.*

This is the only point requiring special attention, for fluorides are formed, and no amount of heating with excess of H_2SO_4 decomposes them unless the heating is continued until H_2SO_4 itself is evolved. By neglecting this no end of trouble may be incurred thereafter by the precipitation of fluorides, and totally erroneous results will be obtained. As the white fumes, towards the finish, may easily be mistaken for H_2SO_4, I invariably test the fumes by holding a gloss rod moistened with dilute NH_4HO in them and dipping it into a test-tube containing dilute acidified $BaCl_2$; no precipitate is given until H_2SO_4 is present. When the crucible has become cold HCl is added and gentle heat applied, until all is dissolved. By covering the crucible with a platinum capsule filled with cold water, which can be withdrawn and renewed by means of a pipette when it becomes warm, condensation of the HCl vapours takes place, all loss by spirting is avoided, and solution hastened. When thoroughly dissolved the acid solution is washed into a beaker, diluted, and the alumina and other ingredients estimated as usual. When precipitating the Al_2O_3, &c., I prefer to colour the solution with litmus, add NH_4HO till just blue, and filter whenever the precipitate settles, thus avoiding all chance of error from the solution of the ingredients of the glass by long boiling, The precipitate is washed with water containing a little NH_4NO_3, until the filtrate is free from SO_3, but, as it may still contain some basic sulphate, it may be re-dissolved. This, however, is unnecessary, as, after ignition for some time at a high temperature over a blowpipe, the precipitate never contains more than immaterial traces of SO_3. This precipitate contains all the Al_2O_3, TiO_2, Fe_2O_3, P_2O_5, and a little Mn_3O_4. The bulk of the manganese, practically all when not much is present, remains in the filtrate, and is precipitated by NH_4HO and bromine-water. CaO and MgO are estimated in the filtrate.

Alkali is estimated by Lawrence Smith's process. By weighing as sulphate, estimating, and deducting the SO_3, the amount of $(KNa)_2O$ is obtained more rapidly than otherwise, and, if required, the proportion of K_2O and Na_2O can be obtained from these data by calculation.

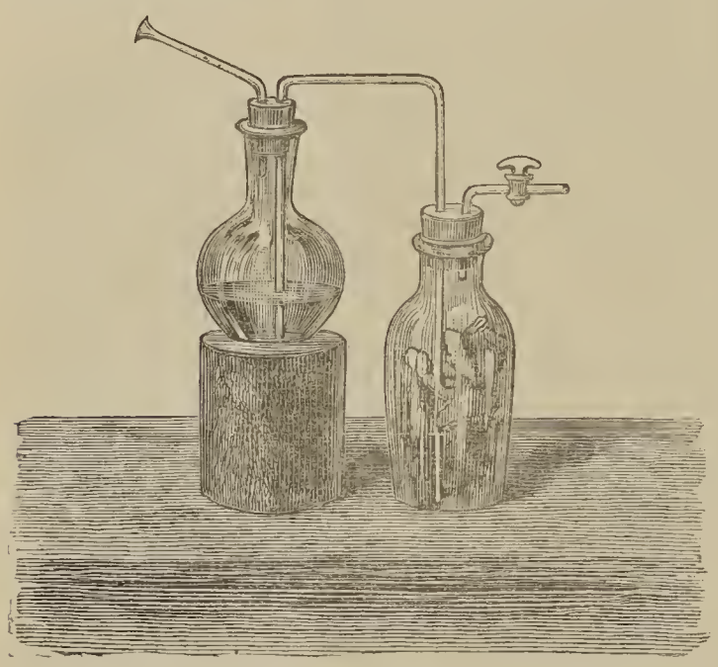
Lugar Iron Works, Cumnock, N.B.

On Horse-Fat.—The weight of horse-fat remains unchanged for about four weeks. In the course of two years the increase due to the absorption of oxygen and the formation of free acids amounts to 3·495 per cent.—*Zeit. Anal. Chem.*, Vol. xxviii., Part 4, 1889.

A SIMPLE SUBSTITUTE FOR KIPP'S APPARATUS.

By EUSTACE THOMPSON.

The accompanying sketch represents a simple contrivance for supplying a continuous and steady stream of carbonic acid. The flask, with a capacity for 500 to 600 c.c., contains hydrochloric acid. The bottle, fitted with a tap-tube, contains chips of marble. They are connected by a tube in the form of a syphon reaching to the bottom of each. The flask is also provided with a tube similar to the shorter tube of a wash-bottle, and for a similar service; it has been represented in its present position for convenience in drawing, but should be turned through 90° towards the reader for convenience in operation. When the evolution of gas is required the tap-tube is opened and the pressure within the flask increased just sufficiently to fill the syphon-tube with acid. Directly acid enters the bottle gas is evolved and more acid flows over. If it is desired to stop the evolution the tap-tube is closed, and the pressure exerted by the gas confined in the bottle rapidly drives the acid into the flask again and empties the syphon. If a steady and continuous stream



of gas is required the opening of the tap-tube can be regulated, with a little trouble, in such a manner that, when once the syphon-tube has been filled with acid, only a small quantity will run into the bottle, because the pressure of the gas, being allowed only limited freedom in egress, is sufficient to prevent an excessive quantity of acid from flowing in. But, as the hydrochloric acid in the bottle becomes saturated with calcium carbonate, its action becomes less vigorous, and the pressure of gas would be diminished but for the fact that additional acid, thus permitted to flow over very gradually, is just sufficient to keep it at the same height.

In the same apparatus the marble may be replaced with zinc or with sulphide of iron for the preparation of hydrogen or of sulphuretted hydrogen respectively. It is, in fact, a simple substitute for Kipp's apparatus. One advantage, not altogether inconsiderable, which gives it a preference to the latter, is, that it requires a far smaller quantity of acid; that which has not dissolved calcium, iron, or zinc chloride remaining in the flask till required, does not mix readily with the portion already saturated, and, when all is saturated, it is very easily replaced by a fresh quantity.

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Bradford Technical College.

EXPERIMENTAL RESEARCHES IN THE REDUCTION OF THE DIFFICULTLY REDUCIBLE METALS.

By A. J. ROGERS.

Aluminium (Al) was probably first obtained by Woehler n 1827 by treating the chloride with the metal potassium, (iK).

Sir Humphry Davy obtained sodium (Na) and potassium (K) in 1808 by the electrolysis of the fused hydroxides of those metals.

He tried to obtain Al by the same method from alumina, but was unsuccessful. Bunsen first obtained minute quantities of the metal by the electrolysis of the fused double chloride of aluminium and sodium (Al_3Cl_62NaCl) in 1854. In the same year, Henry Ste.-Claire Deville first prepared the pure metal in sufficient quantity to be able to study its properties. His process was by the reducing action of Na upon Al_2Cl_62NaCl, using about one-third of cryolite as a flux.

The Deville process has remained, with but slight changes in detail, as the only practical process for the extraction of pure Al. Deville first established a small plant at Javel, France, but later united with Debray, Morin, and Rosseau Brothers. Still later, Merle and Usiglia, in Salindres, gave Deville's process the high perfection that it has to-day. By that process the largest item of cost is the sodium used. In 1852 Na sold at two hundred dollars a pound, but in 1862, by improvements in the process of manufacture, it had been reduced to a dollar and a half a pound. Al_2Cl_6 and Al_2Cl_62NaCl are very hygroscopic, and, when heated in presence of air moisture, hydrochloric acid, and alumina are formed in considerable quantity. During the reduction with Na it is claimed that alumina would form upon the surface of the minute globules of aluminium and thus prevent cohesion between them. Cryolite was used as a flux to assist in removing this oxide. Prof. H. Rose first used cryolite (the double fluoride of sodium and aluminium, Al_2F_66NaF,) as a source of Al. He heated cryolite with Na in an iron crucible, using KCl as a flux, and stirring with an iron rod. His metal, of course, always contained some iron. Rose never obtained more than 80 per cent of the theoretical amount of Al in the cryolite, and many times not more than 33 per cent.

Basset affirmed that all metals will decompose Al_2Cl_6 or Al_2Cl_62NaCl which form chlorides that are more easily liquefied or vaporised than these salts. Hence arsenic (As), antimony (Sb), mercury (Hg), and zinc (Zn) would act as reducing agents of Al. Zinc would seem to be the best from its cheapness and the greater ease of separating from its alloy of Al by distillation of the zinc. According to Basset, the operation consists in heating 3 parts of Al_2Cl_62NaCl with 2 parts of zinc. By stirring, the chloride mass gets denser and finally solid, while the resulting Al alloy remains liquid. This salt mass and alloy are heated to a strong red heat for an hour or more; the molten mass is then stirred with an iron rod, and the salt poured off after the solidifying of the metal. An alloy is obtained consisting of equal equivalents of Al and Zn. Basset's process was recommended by Wedding and others. Specht, in 1860, decomposed Al_2Cl_6 by the use of Zn, and recommended it as the best process in practice.

Dullo states that there is no difficulty in reducing the double chloride with Zn, but it is not as easy as with Na, and the loss of Zn is considerable, and the high temperature required also burns a great deal of Al. My own experience is that the reduction is very incomplete, and only a very small percentage of the Al contained in the salt can be obtained. The Zn process has been more recently experimented upon by F. J. Seymour. He claims to use 100 parts of the Zn ore, 50 parts of kaolin, 125 parts of carbonaceous matter, 15 parts of pearl ash, and 10

parts of NaCl. It is not probable that much Al would be obtained by this process; certainly not pure Al. Petitjean decomposes sulphide of Al by heating in a crucible, through the bottom of which a stream of marsh-gas passes. He also claims to have effected the reduction by mixing the sulphide of Al with iron-filings and igniting. Cumenge ignited sulphide of Al with clay or Al sulphate free from water. Corbelli, in Florence, took 100 parts of clay with 600 parts of H_2SO_4 or concentrated HCl and gradually heated to 500°. This mass is mixed with 200 parts of KCN, 150 NaCl, and heated to a white heat. Deville was unable to obtain Al by this process. Knowles reduced the chloride by KCN, Fleury is said to have produced Al from clay mixed with gas-tar, rosin, petroleum, or similar substances. This was made into a dough and formed into balls, which, after drying, were heated in a tube at a cherry-red heat with marsh-gas under 20 to 30 pounds pressure. The reduced Al, in a fine powder, was melted with Zn, and the Zn afterwards distilled. None of these processes, except Deville's sodium process, have attained any prominence, and it would seem quite impossible to be able practically to reduce Al from its salts or ores by the use of ordinary reducing agents, including the common cheaper metals. Some years ago I commenced a study of some of the problems involved in the production of the difficultly reducible metals from their fused salt by electrolysis. Some results of an investigation of the alkali metals were given in a paper before the Physical Section of the American Association for the Advancement of Science, at its meeting in Ann Arbor in 1885. The principal points stated and conclusions reached in that paper I give in the following summary :— I had observed, according to J. J. Thomson, that the heat of chemical union of one pound (or kilogrm.) of Na with Cl to form NaCl is 4247 centigrade units; while that of carbon (C) with oxygen (O) is about 8000 units. Hence, in the combustion of one pound of C heat enough is obtained to reduce nearly two pounds of Na from NaCl if the heat energy could be utilised without loss. But no purely chemical method has even yet been suggested by which this kinetic heat energy of the coal, or C, can be transformed without loss into potential energy of separation of the Na and Cl in NaCl. If electrical energy can be applied without loss to produce the separation of NaCl into its constituent elements, we can easily compute the amount of coal used in a steam-engine to give the necessary amount of electric energy in the dynamo machine to produce a given amount of Na. Thus one mechanical horse-power per hour is equivalent to about 1425 heat units (pound degrees centigrade), and therefore this energy transformed without loss into electrical energy, and this electrical energy again into chemical work in decomposing NaCl, would give us (4247 divided into 1425) nearly one-third of a pound of Na per horse-power per hour, or 8 pounds a day of twenty-four hours. In practice, one mechanical horse-power applied to the dynamo machine generally yields not more than 80 to 90 per cent of one electrical horse-power. Thus, if there were no transfer resistance in the passage of the electric current through the molten NaCl electrolyte, but all the energy of the current were changed into chemical work, from 6 to 7 pounds of sodium would be set free at the negative electrode in twenty-four hours. Again, the electro-chemical equivalent of Na is 0·000238 grm., *i.e.*, with one ampère of current that amount of Na should be deposited at the negative electrode in one second of time, 0·8568 grm. would be deposited in one hour, or 20·56 grms. in twenty-four hours. Hence, 178 ampères would be required to deposit 8 pounds of Na in twenty-four hours. Since there are 746 watts to one electrical horse-power a voltage of (746 divided by 178) 4·2 would be necessary.

F. Exner (*Wiedemann's Annalen Band*, vi., Seite 353) gives the potential difference of Na and Cl at 2·06 to 2·08 Daniells, which would indicate, if correct, under our given conditions, a deposit of nearly twice 8 pounds in twenty-four hours. In a similar manner I computed what should be the theoretical value for the amount of deposit of other difficultly reducible metals in the electrolysis of their fused salts. It seems probable that the electrolysis of NaCl and allied salts can never be carried on successfully in any aqueous or other ordinary solutions, on account of the secondary products that are formed by the action of the liberated ions. So it would seem that the salt must be rendered liquid by fusion. The temperature of fusion may be lowered considerably in many salts by the presence of other salts, *e.g.*, NaCl melts at 200° below its ordinary melting temperature (776° C., according to Carnelley) in the presence of a small amount of $CaCl_2$, and its temperature is considerably lowered by the presence of a small proportion of KCl. In my experimental work various kinds and forms of crucibles and electrodes were used without my being able to obtain very much pure metal. But my intent was mainly to get some quantitative results as to the amount of deposition of metal at the cathode. For measuring strength of current, water, silver, and copper voltameters, of my own construction, were used, as also a tangent galvanometer, whose reduction factor had been carefully determined. The following results, among many others, were obtained, at the time using a Grove battery, for electrical power, a Battersea crucible for containing the NaCl, a carbon anode, and an iron cathode terminating in a tube of lime placed in the melted salt. As soon as metallic Na was seen to escape and burn at the surface of the liquid, the current was stopped, liquid cooled, crucible broken, and the amount of Na determined by a standard acid solution. Some of the Na was oxidised, while a considerable amount would be found in the tube in the pure metallic state.

Exp.	Ampères.	Time in seconds.	Observed amount Na. Grm.	Theoretical amount Na. Grm.
1.	3·2	90	0·04	0·066
2.	2·5	480	0·14	0·286
3.	2·8	360	0·16	0·24
4.	2·8	300	0·17	0·20
5.	3·5	420	0·2+	0·36
6.	2·0	480	0·13	0·22

The loss can be accounted for from the escape of some of the volatilised Na into the air and from diffusion and re-composition with the liberated chlorine. The resistance, measured by the method of substitution, varied from 1 to 1·5 ohms, with an average of about 1·3. Four large chromic acid cells were used in series in much of the work. It thus seemed that, with suitable apparatus, from 5 to 6 pounds of Na could be produced in twenty-four hours to one electrical horse-power. Thus, if there were no practical difficulties in the construction of crucibles and other apparatus involved, nor in working continuously on a large scale with a raw material so cheap and pure as NaCl, the metal could be obtained at small cost, and could be applied to the reduction of other difficultly reducible metals, including that very valuable metal Al. Various forms of crucibles were used and attempts made to distil the metal when formed at the negative electrode. Na volatilises at near 900° C., and when obtained from the electrolysis of NaCl, carries with it a large amount of vapour of NaCl, so that distillation is attended with some difficulties. Small specks of Al were also obtained by direct electrolysis of Al_2Cl_62NaCl, and of Al_2F_66NaF, but only a small percentage of the theoretical yield could be obtained.

Since the preparation of the paper of which the preceding is an outline, I have given attention more particularly to the direct electrolysis of salts of Al, using different salts of the metal with different fluxes, and different forms and materials for crucibles and electrodes. Some of the many points to consider in attempting to obtain Al by the direct electrolysis of its salts are the following :—

1. Cheapness of the salt or material used.

2. A salt whose melting-point is above the melting-point of the Al, and boiling-point below that of Al.

3. That will to the least extent attack the material of the crucible and electrodes.

4. Which offers the least transfer resistance.

5. Which does not dissolve the metal when once liberated at the cathode.

6. That does not facilitate diffusion of the ions and thus permit their re-uniting.

The salts that have been found in practice necessary to use are the anhydrous chlorides and fluorides of Al; more commonly the double salts with sodium. The double chlorides, as given in Hofmann's reports for 1872, cost at the factory in Salindres, France, 22 cents per pound, which would make its cost for a pound of Al 2·20 dols. The Webster-Castner works, at Oldbury, near Birmingham, now have facilities for manufacturing the double chloride in much larger quantities than heretofore, and have undoubtedly made improvements in minor details; but the general process remains the same as it was in 1872, and no great reduction in cost can be expected. The double chloride can be made quite free from silicon (Si), but always contains some iron (Fe). Cryolite is necessarily used as a flux when the double chloride is reduced by Na. The action of the cryolite has been explained as dissolving the thin coating of oxide that forms around the reduced particles of Al.

It may be, however, that the action of the cryolite is not that of a solvent of the oxide of the metal simply, but that it assists in decreasing the surface tension of the minute globules of metal, or otherwise mechanically causing them to cohere. The native double fluoride (cryolite) can be obtained much cheaper than the double chloride.

From the Government reports of mining and mineral statistics, the amount of cryolite imported into the United States is from 5000 to 8000 tons per year, at a cost of about 15·00 dols. per ton. This cost, the Pennsylvania Salt Co. (who control the cryolite business in this country), have told me is incorrect and too low.

They sell what they call pure cryolite at 125 dols. per ton, or 6·5 cents per pound. This would make the cost of an amount sufficient for one pound of Al 65 cents, supposing the yield of Al is 10 per cent of the salt (theoretically nearly 13 per cent). This so-called pure cryolite from the Pennsylvania Salt Co. contains, I find, 2 per cent of silica and 1 per cent of Fe. I am confident that the artificial fluoride can be prepared at half the cost and of much greater purity than the natural cryolite.

(To be continued).

PROCEEDINGS OF SOCIETIES.

PHYSICAL SOCIETY.

November 1, 1889.

Prof. Reinold, F.R.S., President, in the chair.

Mr. T. A. Garrett was elected a Member of the Society.

The following communications were read:—

"*On a New Electric Radiation-Meter.*" By Mr. W. G. Gregory.

The meter consists of a long fine platinum wire attached to a delicate magnifying spring of the Ayrton and Perry type, and stretched within a compound tube of glass and brass. At the junction between the wire and spring a small mirror is fixed. When the tube is placed parallel to a Hertz's oscillator in action, the mirror is turned in a direction indicating an extension of the wire. The arrangement is so sensitive that an elongation of 1·200,000th of an m.m. can be detected. This apparent extension is such as would correspond to a change of temperature of 0·003° C. By its aid the author has roughly verified Hertz's statements that at considerable distances the intensity of radiation varies as the inverse distance but before he can proceed further it is necessary to greatly increase the sensibility of the apparatus; and with a view of obtaining some suggestions in this direction he exhibited it before the Society.

Prof. Perry asked if the E.M.F. required to produce the observed results had been calculated; he also believed that the sensibility might be increased by using copper instead of platinum, and replacing the spring by a twisted strip.

Mr. Blakesley enquired whether the effect of increasing the capacity of the ends of the wire had been tried.

Mr. Boys said if the observed effect was due to rise of temperature he would like to see it measured thermally. He also thought the effect might be due to extension caused by rapid electric oscillations in some such way as the elongation of an iron bar caused by magnetisation.

In answer to this Prof. S. P. Thompson said the matter had already been investigated experimentally, but with negative results.

Prof. Herschel suggested the use of a compound spring, such as are used in Breguet's metallic thermometers.

In reply Mr. Gregory said he had estimated the E.M.F. by observing that a Lechlanchè cell through 50 ohms produced about the same result. No improvement in sensitiveness was obtained by using copper wire or by increasing its capacity, and attempts to measure the rise of temperature by an air thermometer had been given up as hopeless.

The President, in thanking the author for his paper, congratulated him on the ingenuity and courage displayed in producing an apparatus to measure such microscopic quantities as are here involved.

"*On a Method of Driving Tuning-Forks Electrically.*" By Mr. Gregory.

In order to give the impulses about the middle of the stroke, the fork is arranged to make and break the primary circuit of a small transformer, the secondary circuit of which is completed through the electro-magnet actuating the fork. The prongs of the fork are magnetised and receive two impulses in each period.

Another device was suggested where the prongs respectively operate contacts which successively charge and discharge a condenser through the coils of the actuating magnet.

Prof. S. P. Thompson said the methods, if perfect, would be of great service, and suggested that a fork so driven be tested optically by comparison with a freely vibrating one. He regarded the mercury contacts used as objectionable, for their capillarity and adhesion would probably cause the impulses to lag behind the appointed epochs.

Prof. M'Leod remarked that Lissajou's figures gave a satisfactory method of testing the constancy of period, and could be readily observed without using lenses, and, in reference to liquid condensers suggested by the author for his second device, said that platinum plates in sulphuric acid were found to disintegrate when used for this purpose. He thought lead plates would prove suitable.

Prof. Jones, who read a paper on a similar subject in March last, said he now used bowed forks with which to synchonise the speed of the disc there described, and the frequency is determined by causing the disc to complete the circuit of his Morse receiver once each revolution.

"*On a Physical Basis for the Theory of Errors.*" By Mr. C. V. Burton, D.Sc.

After pointing out that the law of error for any particular measurement depends on the nature of the conditions governing such measurement, the author considers several simple cases and deduces their curves of error. A kinematic method of combining two or more independent errors, each following known laws, is then described and applied, and the general formula obtained leads to

Laplace's law of error in the case of an infinite number of similar errors.

Referring to *Most Advantageous Combinations of Measures*, it is shown that the method of least squares is only a particular solution of the general equation, and is derived by assuming the individual errors to conform to Laplace's law.

Subjective Errors are next considered, and in conclusion the author says that "the law of error in a set of observations depends on the nature of each special case, and what may be called the probable law of error is determined by our knowledge of the conditions. The combination of three or more sources of error of comparable importance gives, in general, a law not seriously differing from that of Laplace, so that the method of least squares will be practically the most advantageous, except where a single source of error with a very different law is predominant above all the rest."

"*A Note on the Behaviour of Twisted Strips*," by Prof. J. Perry, F.R.S., had been prematurely announced by mistake, and he accordingly gave only a brief outline of the paper.

In a previous communication Prof. Ayrton and the author enunciated a working hypothesis, in which the strips were imagined to be split up into pairs of filaments, each pair acting as a bifilar suspension. The resulting formula for the rotation produced by a given load did not agree with experiment, and quite recently the author had recognised why the formula was incorrect. The bifilar law they had assumed was only true for small twists, but he now saw another method of treatment by which he hoped to verify the formula derived from experiment before the next meeting.

Prof. Fitzgerald reminded Prof. Perry of a method of attacking the problem suggested by the speaker some time ago, in which each filament was supposed to be wrapped round a smooth cylinder, and said that on working it out the formula was found to be very complicated.

Mr. Trotter thought the pairs of strips might be regarded as twisted ladders, and

Mr. Gregory said this suggestion reduced the problem to a series of bifilar suspensions, which had already been worked out.

"*On Electrifications due to Contact of Gases and Liquids.*" By Mr. J. Enright.

For some time past the author has been studying the electrical phenomena attending solution by connecting an insulated vessel in which the solution takes place with an electrometer. As a general rule, no effect is observed if nothing leaves the vessel, but when gases are produced and allowed to escape the vessel becomes charged with + or − electricity, depending on the nature of the liquid from which the gas passes into the air. As an example, when zinc is placed in hydrochloric acid the deflection of the electrometer is in one direction whilst the liquid is chiefly acid, but decreases and reverses as more and more zinc chloride is produced. From such observations the author hopes to obtain some information relating to atomic changes.

Owing to the lateness of the hour the latter portion of the paper and the discussion on it were postponed until next meeting.

ROYAL INSTITUTION OF GREAT BRITAIN.

General Monthly Meeting, Monday, November 4, 1889.

Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—Thomas Browning, C.B.; Latimer Clark, F.R.S., M.Inst.C.E.; Charles Pitfield Mitchell, M.R.C.S.; Maurice Powell, M.A.; and Delisle Powles.

Edward Pollock was elected a Manager of the Royal Institution in the room of Sir James Crichton-Browne, M.D., resigned; and James Edmunds, M.D., F.C.S., was elected a Visitor in the room of Edward Pollock, resigned.

The Special Thanks of the Members were returned to Professor Dewar, F.R.S., for his valuable present of a Portrait of the late Mr. Henry Pollock.

The Special Thanks of the Members were returned to the Rev. John Macnaught, M.R.I., for his second donation of £50 for improvements in the Building.

The Presents received since the last Meeting were laid on the table, and the thanks of the Members returned for the same.

NOTICES OF BOOKS.

Laundry Management: a Handbook for Use in Private and Public Laundries; including Descriptive Accounts of Modern Machinery and Appliances for Laundry Work. By The Editor of *The Laundry Journal*. With numerous Illustrations. London: Crosby Lockwood and Son.

The day of small things is over, no less decidedly in the industrial arts than in States. Everything, to stand its ground against constant competition, must be conducted on the large scale. Articles which, within the memory of persons now living, were made in the back shops of the vendors, are now prepared on a vast scale in extensive specially constructed buildings with the aid of steam-power. The laundry was, till lately, an outhouse in country seats, a room in dwellings of humbler pretensions, serving also as the scullery, or perhaps the cottage of some industrious woman reduced to "take in washing."

Now, washing, in the neighbourhood of our large cities at least, has become a special business in which considerable capital is invested, and which is no longer carried on by rule of thumb.

The work before us, compiled by the Editor of the *Laundry Journal*,—a paper whose very existence is significant of the change which has taken place—seems to us to cover the whole field. It begins with a chapter on sorting and marking linen. Under this head we find a caution against the corrosive action of many marking-inks.

Next follows the important subject of disinfection. It is well known that many persons, who have small conveniences for washing and drying at home, yet prefer to have the house filled, weekly or fortnightly, with clouds of steam rather than run the risk of their clothing coming in contact with linen from a house where small-pox, diphtheria, or scarlet fever may be raging. The author is fully alive to the difference between true disinfectants and mere deodorisers, or maskers of evil smells.

Condy's fluid the author considers rightly objectionable, on account of its colour and the stains it leaves upon textile fabrics. He seems to be of opinion that Californian borax contains more boracic acid than that from any other source. This is an error; genuine borax, wherever it has been manufactured, and whatever may be its original source, contains one and the same proportion of boracic acid. He prefers, however, disinfection by means of hot air or steam, giving the precaution that the latter will injure many colours.

Water is the next question. As a matter of course, he condems hard waters as injurious, in the long run, to the goods washed, and as distinctly uneconomical. He recommends the Clark process, which is worked with such success on the water-supplies of Canterbury, Aylesbury, and Tring.

The caution that salts and soaps of soda should never be brought in contact with woollen tissues, now so thoroughly understood by wool-dyers, is not here given.

The question of adulterated soaps is discussed at some length. This is an evil which the public has brought upon itself by its rage for ostensible cheapness. There is, however, abundance of genuine honest soap in the market; the qualities most advertised being, as a rule, most to be suspected.

Soap-powders and soap-substitutes the author views with suspicion, and chloride of lime, he thinks, had much better be kept out of the laundry altogether. It is anything but pleasant to sleep between sheets which have been saturated with hypochlorites, troubling your rest with visions of St. Helens and Widnes. He denounces warmly, but justifiably, laundries which do a "cutting" trade, pay starvation wages, and make use of corrosive chemicals.

In the chapter on "blueing," the author says that ultramarine, "properly manufactured, is easily soluble"; a strange assertion.

The chapter on cleaning, renovating, and dyeing feathers, gloves, &c., seems rather out of place in a laundry handbook. There is also a section on carpet-beating open to the same objection.

Viewed as a whole the work must be pronounced useful to the trade, and beneficial to the the public, if its lessons are carried out.

Practical Photometry: a Guide to the Study of the Measurement of Light. By W. Jos. Dibdin, F.I.C., F.C.S., &c. London: Walter King, Office of *Journal of Gas Lighting*.

The art of photometry has latterly assumed great and increasing importance, and it is not too much to say that in the practice of this art Mr. Dibdin has come to the front in a very useful manner. Hitherto, we believe, there has not existed any guide-book to which the photometist might refer in novel and difficult cases. Such cases have of late become more frequent in consequence of the introduction of the electric light, and of burners which send down their rays at all angles. Under such circumstances, the work before us will generally point out the expedient to be adopted.

Mr. Dibdin begins with the history of photometry, which may, in reality, be said to have commenced with the felt necessity of keeping a check on "keen questioning directors." Says Mr. Dibdin:—"He (the gas maker) undertakes to supply a certain article for a certain price, and he can no more be expected to exceed that bargain than can the family butcher be asked to add an odd ounce or two to every pound of beef that he sells." We never heard of any person simple enough to entertain such expectations. But both gas maker and butcher, unless sharply watched, will fall below their bargain, and the gas maker being not, like the butcher, liable to competition needs a very close inspection. Why, otherwise, have gas examiners at all?

The mean value of the Carcel lamp, used as the standard in France, is given as 9·5 English normal candles. At the recent Congress of Electricians sitting in Paris it was recommended that our candle should be reduced in value so as to be exactly 0·1 Carcel. But if, as the author recommends, and as we certainly think it desirable, the pentane air-gas of Mr. A. G. Vernon Harcourt is adopted as the legal standard of reference, we need not trouble ourselves about any modification of the candle.

The next chapter treats of the principles of photometry. Here we find especial attention called to the influence of burners upon the results. At present, thanks to the legislature, the photometrist, before beginning to test, has to select a burner prescribed for the particular quality of gas. This system Mr. Dibdin very rightly pronounces confusing, and recommends its abandonment.

Much of the chapter is taken up with an abstract of an important paper read by Messrs. Heisch and Hartley before the Gas Institute in 1884.

In Chapter III. we find a discussion of "Horizontal Photometers." The author drily remarks that:—"The traditional way to make a 'new' photometer is to alter the wooden casing as much as possible and then to call this outcome of the cabinet maker's art a new photometer."

The form of the instrument here described, and mostly figured, are the King's, the Lethel, the Canadian, Keats's candle balance, the closed Evans, the open Evans, the Imperial, the Harcourt's Table, and the Portable.

We next come to the so-called radial photometers, which determine not merely the illuminating power of the rays falling horizontally, but of those falling at all angles from the horizontal to the vertical. Here we have Hartley's "universal" photometer, the author's own instrument, the radial, Sugg's travelling photometer, and the Lolophotometer.

After the description of these instruments comes an account of the two forms of discs, the Bunsen and the Leeson. Mr. Dibdin considers that the former, a greased disc, is unsatisfactory for testing electric lights or recuperative gas-burners, and has therefore abandoned it in favour of the modified Leeson.

Under "Standards of Light" comes an account of the English sperm candle, the French Carcel lamp, and the German paraffin candle, each of which has its shortcomings.

Among the proposed substitutes, Violle's solidifying platinum is rejected as not practical, whilst the Harcourt system, referred to above, is proposed as the standard of the future.

The amyl-acetate lamp (Von Hefner-Altenecks) is open to objection on account of its dusky flame.

The chapter on "Colour Photometry," is, perhaps, of questionable relevance in a work dealing with the values of sources of light. It contains a notice of Lovibond's tintometer, an instrument likely to supersede the old colorimeter. Although it was first made known in a paper read before the Society of Dyers and Colourists, it does not seem to have come into extended use in the tinctorial arts.

Stellar photometry, which forms the subject of the final chapter, is exceedingly interesting, though to routine gas makers and gas examiners it will seem out of place and unpractical.

An appendix contains the notification of the gas referees for the summer of the current year, the times and modes of testing for illuminating power, and for impurities, the limits for sulphuretted hydrogen, for ammonia, and for sulphur-compounds other than with hydrogen. Then follow figure and description of Sugg's London Argand burner, the gas referee's street-lamp pressure guage, table showing correction of volume of gas at different temperatures and pressures, blank forms of examiner's reports, gas referee's cubic foot measure, revised regulations as to gas-measuring standards, apparatus for testing gas meters, gauges for connecting pipes and fittings, proposed Board of Trade standards for gas-meter connection pipes and fittings, weight of oil burned hourly in Carcel lamp, and tables for candle corrections, and for the illuminating power of sperm lamps.

Mr. Dibdin's work must be pronounced not merely useful, but essential to all persons who are engaged in manufacturing, selling, or checking gas, and no less to those concerned in the introduction of the electric light.

The Air inclosed in the Soil.—Th. Schlœsing, Jun.—The author's results verify the fact of the abundance of oxygen in the ground air. The sub-soil, also, is in general well supplied with this gas. Save in exceptional cases, it cannot be said to have a reducing atmosphere. The composition of the gases collected is not alike at all times. In sloping ground carbon dioxide is not abundant at the lowest points.—*Comptes Rendus*, Vol. cix., No. 16.

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—As Herr Wollheim now does "not for one moment dispute that other sludges may be inoffensive, even when first drawn from the tank," he, in fact, concedes all that I could desire. Sewage precipitates, of any manurial value, do not require to be left exposed for weeks to rain and sunshine, as they can be readily turned to better account.—I am, &c.,

The Writer of the Report.

MILK ANALYSIS.

To the Editor of the Chemical News.

Sir,—I have read with extreme interest Dr. Bennett F. Davenport's article upon milk analysis, which appeared in the Chemical News (vol. lx., p. 213). I thoroughly agree with him in all that he has written concerning the estimation of the fat in milk; the process employed being termed by him a modified Wanklyn. I am in the habit of using platinum basins of 2½-inch diameter but having quite flat bottoms, and have no difficulty whatever in obtaining a very thin and evenly distributed skin of residue; the complete extraction of which, by means of petroleum ether, is easily accomplished. Petroleum ether, as mentioned by Dr. Davenport, having a great advantage over that of ether in not dissolving either lactic acid or lactose.

The process known as the "Adam's blotting-paper," and recommended by the Milk Committee of the Society of Public Analysts, is a process which is decidedly faulty, and that in three respects, and my reasons for saying so are as follows:—First, you cannot estimate directly both the fat and the solids not fat. Second, that the amount of fat obtained is in excess of that originally present in the milk, owing to an increase in weight due to rapid oxidation of the fat when in contact with cellulose, when spread over such a large surface, and also to a further oxidation which takes place when completing the drying of the extracted fats in the water-oven. Third, it cannot be used when the milk is not fresh, objections which are fatal to any milk process, and which, by unprejudiced persons, connot be gainsaid.

I used blotting-paper in milk analysis in 1882 (before Mr. Adams) and relinquished its use, owing to the last objection, and, finally, by a long series of experiments, satisfied myself as to the correctness of my second objection, and when coupling that with the first and third objection I have now no hesitation in rejecting it as faulty.

My opponents may say that the fat calculated from the sp. gr. and total solids agrees that found by Mr. Adams's process, but to that I reply we have already had examples of altering formulæ to suit the particular process employed.—I am, &c.,

William Johnstone.

City Central Laboratory,
13, Fish Street Hill, E.C., Nov. 4, 1889.

MILK ANALYSIS.

To the Editor of the Chemical News.

Sir,—In an article on "Milk Analysis" in the Chemical News (vol. lx., p. 213) Dr. B. F. Davenport states that the fat can be *entirely* extracted from the dried residue of 5 grms. of milk if only this be in a flat-bottomed platinum dish of 2½ inches diameter. He uses four separate quantities of boiling benzine. Unluckily he gives no comparative analyses to show that the fat is *entirely* extracted

For years I used exactly the method described, sometimes with larger flat-bottomed dishes, and always with more numerous changes of benzine, boiled on the residue. The fat, however, was never entirely separated, nor even to within "one-tenth of a per cent." In a paper in the *Analyst*, February, 1889, he will see this method contrasted with more modern methods. In my experience there are only four methods that extract all the fat from a milk:—1st, Soxhlet's areometric method; 2nd, Soxhlet's tube with pumice, plaster-of-paris, kieslguhr or paper-coil (Adams); 3rd, the lactocrite; 4th, the Schmid method. This last was described in the Chemical News, vol. lx., p. 214.—I am, &c.,

A. W. Stokes, F.C.S., F.I.C.

Analytical Laboratory,
Vestry Hall, Harrow Road, W.,
November 4, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 16, October 14, 1889.

Reciprocal Displacements between the Halogens and Oxygen; the Hydrobromic and Hydriodic Acids.—M. Berthelot.—A thermo-chemical paper, not adapted for useful abstraction.

New Relations between the Sugars and the Furfuric Compounds; Constitution of Methylfurfurol and Isodulcite.—M. Maquenne.—If isodulcite is distilled with four parts by weight of sulphuric acid, of sp. gr. 1·109 to 1·152, we obtain an aqueous liquid smelling strongly of furfurol, which precipitates slowly on the addition of ammonia, and gives with phenylhydrazine acetate an insoluble and non-crystalline hydrazone. This liquid, if fractionated, gives off first a little acetone and then a dense yellowish oil, which passes over entirely between 186°—187°. This oil consists of pure methylfurfurol, identical with that obtained on the distillation of sea-weeds, and consequently with that from wood-tar.

The Fermentation of Raffinose in presence of various Beer Yeasts.—D. Loiseau.—The author refers to matter contained in a "sealed paper" deposited with the Academy, March 5th, 1888, some of which is not yet ready for publication. Raffinose ferments completely in presence of beer-yeast, from a "bottom" fermentation, yielding theoretical quantities of alcohol and carbon dioxide. With yeast from a "top" fermentation the process is incomplete, only about one-third of the normal quantities of alcohol and carbon dioxide being obtained; whilst there remains in the fermented liquid a substance which reacts upon Fehling's liquid, which ferments completely with bottom yeast while resisting top yeast.

Observations on M. Guignet's Communication of September 30th.—MM. Vincent and Delachanal.—M. Guignet states that he has been able to extract well crystallised mannite from the cupric precipitate obtained from a decoction of sea-weed and from the juice of mountain-ash berries before the separation of the sorbite. The authors find that sorbite is completely precipitated by M. Guignet's reagent. The production of this precipitate does not warrant us in inferring the presence of mannite in the juice of mountain-ash berries, nor its separation from sorbite.

The Optical Analysis of Oils and Butter.—E. H. Amagat and Ferdinand Jean.—This paper will be inserted in full.

Journal de Pharmacie et de Chimie.
Series 5, Vol. xx., No. 4.

On the Possibility of Communicating the Bouquet of a Wine of High Quality to a Common Wine by Changing the Ferment.—A. Rommier.—It appears that the flavour of a wine depends less on the nature of the soil in which the vines have been grown than on the ferment employed. The wine-ferments, which have been hitherto supposed identical and which have received the name *Saccharomyces ellipsoideus*, are various, and communicate different qualities to the must in which they set up fermentation. The juice of the "chasselas" grapes of the South of France can, by a change of ferment, be made to yield high-class (*grands crus*) Burgundies.

Detection of Saccharine in Mixtures.—Introduce into a flask about 20 grms. of the substance in question with an equal volume of water, and shake it up. Add 5 drops of sulphuric acid, shake, and pour in a volume of ether equal to that of the mixture; shake very gently to prevent the formation of an emulsion. After settling draw off the ether by means of a decanting-tube, evaporate it to dryness, and taste the residue. If saccharine is present it will have an intensely sweet taste. The evaporation of the ether must, of course, be conducted in the absence of fire or flame.

Reactions of Furfurol and their Utilisation for the Detection of Certain Organic Compounds, Amylic Alcohol, Alkaloids, &c. — L. von Vdranzky. — The author has studied a great number of substances. Among those which give coloured reactions in presence of furfurol and sulphuric acid some are coloured in the same manner, whether treated with sulphuric acid alone or with this acid and furfurol. Other bodies are coloured only when both reagents are employed, or at least the colour which they give with sulphuric acid alone is not the same as that produced by the joint action of sulphuric acid and furfurol.

Colours Produced by Furfurol and Sulphuric Acid.

Acetacetic ether ..	Red.
Acetone	Light cherry red.
Aniline	Bright red.
Anthracene	Greenish, then red, then blue.
Anthraquinone	Light red.
Atropine	Light rose.
Borneol	Peach-blossom, then violet, then blue.
Brucine	Light violet.
Cholesterine	Bright red and then blue.
Cinchonine	Light rose.
Coumarine	Light violet.
Dimethylaniline ..	Light rose.
Cresol	Light red, then violet, and then blue.
Ethylenic glycol ..	Bright raspberry red.
Malic acid	Light rose.
Methylic alcohol ..	Light cherry red.
Morphine	Raspberry red, then bluish.
Naphthol α	Splendid violet.
Phenanthrene	Violet.
Phenol	Cherry red, then blue.
Phenylhydrazine ..	Cherry red.
Phloroglucine	Raspberry red.
Protocatechuic acid ..	Violet, turning blue.
Pyrogallol	Bright cherry, then violet.
Quinic acid	Light violet.
Salicylic acid	Light rose red.
Strychnine	Dirty violet.
Tyrosine	Faint rose red.
Vanillic acid	Light rose red.

The method of applying the reagents is as follows:—A particle of the substance, if solid, or a drop if liquid, is put in a test-tube with 1 c.c. of water or alcohol, a drop of furfurol water at ½ per cent is added, and about 1 c.c. of strong sulphuric acid is carefully let run in down the side of the tube. The bottom of the tube is kept in a current of cold water so that the temperature may not exceed 50°. In some cases, besides the colouration mentioned above, there is observed the formation of a green band. Some of the coloured liquids present peculiarities if examined with the spectroscope. This is the case with naphthol α; if examined after agitation there is a narrow band, not well defined at equal distances, between D and E. After F the spectrum is obscured. With ethylenic glycol we see two very definite bands, a broader one at E and a narrower one at F.

MISCELLANEOUS.

The Cornish Uranium Mine.—It is gratifying to find that a continuous lode of uranium ore—unique in the world—has been met with in the parish of St. Stephen's, Cornwall, about 1½ miles distant from Grampound Road. The lode varies in width from 3 to 5 feet, and the uranium ore is not distributed in bunches or pockets, as is the case elsewhere, but is continuous throughout. This valuable metal, worth at present about £2400 per ton, occurs in the state of uranic phosphate, though hydrated uranous oxide is also to be met with. Samples of the ore seem to have yielded, on the average, 12 per cent of the pure metal, though some samples run up to 30 per cent. The advantageous feature of this deposit of uranium ore, in addition to its continuous character, is its freedom from arsenic and other ordinary impurities, which render the extraction and purification of the metal difficult and costly. Our readers are, of course, aware of the uses of uranium, in giving green and golden colours to glass, in the production of a fine black upon porcelain, and in photography. But if a large and regular supply is available it may be used in electro-plating, and in the formation of gold-coloured alloys with platinum and copper, the former of which is said to resist acids. This may open the door at once to honest and dishonest arts.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Calcined Caustic Lime.—A correspondent wishes to know where this can be obtained in large quantities.—T. H.

Analysis of Cocoa, &c.—Can any reader refer me to papers or books which would help me in the analysis of cocoa, chocolate, and other confectionery?—Analyst.

MEETINGS FOR THE WEEK.

Friday, Nov. 15.—Physical, 5. "On Electrification due to the Contact of Gases and Liquids," by J. Enwright. "On the Effect of Repeated Heating and Cooling on the Electrical Resistance and Temperature Coefficient of Annealed Iron," by H. Tomlinson, F.R.S. "Notes on Geometrical Optics, Part II," by Prof. S. P. Thompson, D.Sc.

FOR SALE. — The Chemical Gazette. Complete Set (unbound and uncut), 17 volumes; from November, 1842, to December, 1859.—Address, "Publisher," Chemical News Office, Boy Court, Ludgate Hill London, E.C

TO BE SOLD, the Lancashire Manure COMPANY'S WORKS at Widnes, with Machinery and 4,420 square yards of Freehold Land.—Address, J. Hosking 16, Fenwick Street, Liverpool

THE CHEMICAL NEWS.

Vol. LX. No. 1564.

DIMIDIUM:

An Attempt to Represent the Chemical Elements by Physical Forms; with Models of the Elements, from Hydrogen to Nickel, constructed in accordance therewith.*

By Dr. ISAAC ASHE.

The author pointed out that when the combining weight of an element was divided by the number representing its combining power, or valency, as compared in both cases with hydrogen, the quotient in many cases presented the fraction one-half, instead of an integer number; and that in many other cases, particularly in the triad series, an integer quotient with unity for a remainder was to be obtained by doubling the combining weight before dividing.

Hence he inferred that an element having half the weight of hydrogen would be found to be the primordial element out of which the other elements were constructed. This hypothetic element he proposed to call dimidium. The number of atoms of dimidium which would go to form any given element would be double the number representing the combining weight of that element as compared with hydrogen. Dimidium itself might probably consist of a number of vortex rings—according to Sir W. Thomson's theory—placed one on the top of another, thus forming an elongated circular bar; a limit would be placed to the length of the bar so compacted, in consequence of a point being reached on each side of the centre, in a lengthwise direction, where the forces of attraction and repulsion between the rings balanced each other. Possibly the hollow tube thus formed might itself be filled with some still lower form of matter, out of which the vortex rings themselves might have been made, perhaps perfect spheres, to which Mr. Crookes's term "protyle" might be applied.

Assuming, then, the existence of this primordial linear element, and representing its atoms by small metallic bars of brass wire, the author showed that—taking in each case the number of bars indicated as above, by doubling the combining weight of each element—he had been able to construct a series of models of the chemical elements, in which their combining power, their positive or negative condition, and their modes of combination, were all expressed, as well as their combining weight. He further shewed that the forms brought out in these models corresponded with the crystalline forms known to belong to certain of these elements; and how the phenomenon of the expansion of water when freezing might be explained by reference to the form employed for the molecule of that compound, which was hexagonal in its general outline.

The forms adopted for the elements in these models were also shown to correspond with the arrangement of the elements in series by Newlands and Mendeleeff, elements belonging to the same series having corresponding forms.

The author suggested that simple geometrical forms, that is to say, the equilateral triangle and the square, were the combinations into which the primordial element would first have entered, and all the models were accordingly constructed out of these forms, along with the simple bar. Thus, the atom of hydrogen was constructed of two single bars placed side by side, and the molecule of four, and he suggested that these were probably separated in the gaseous condition, so as to form a hollow cube. There were other secondary forms constructed out of the triangles and squares, and the models of many of the elements were then constructed out of these secondary forms.

Lithium was formed of two squares and two triangles, or 14 pieces, its combining weight being 7. Carbon was formed by placing two pyramids base to base, each pyramid being formed of four equilateral triangles, in all 24 pieces, its combining number being 12. The crystalline forms, both of the diamond and of graphite, were shown to correspond with this, the former being made by placing a number of the carbon atoms together by their edges, and the latter by placing them in apposition by their triangular facets.

Silicon was formed by replacing each of these triangles by a group of seven, formed of two triangles united at their bases and separated at their vertices by a single bar component. This was shown to correspond with the crystalline forms of silicon.

Sodium and potassium were so constructed as to correspond with the form adopted for lithium, these being all members of the same series. Similarly, magnesium and calcium were so constructed as to correspond with beryllium, phosphorus and vanadium with nitrogen, sulphur with oxygen, chlorine with fluorine, &c.

Iron, and the group of tetrad elements analogous with it, were constructed out of a common base form consisting of 88 components, to which pairs of secondary forms, consisting of 20, 22, and 24 components respectively, were added to represent chromium, manganese, and iron respectively. The forms adopted for all these elements corresponded with that representing aluminium, so that the replacing of an atom of this latter element by one of any of the former in the alum compounds was shown to be in accordance with the theoretical forms assigned to these elements.

The author suggested that probably metals combined with non-metals by lateral interpenetration, a salient angle of the former corresponding with a re-entrant angle of the latter; but that two non-metals combined by superposition, corresponding angles being applied one to the other. The union of boron with nitrogen at a high temperature was shown, by reference to the models, to be an illustration of this view. The compounds of oxygen with nitrogen and with chlorine were also discussed, and a corresponding explanation of them suggested. What is known as the nascent condition of elementary atoms was explained as consisting in a sliding movement between two atoms which had been combined, so that one of these was removed gradually from the other, while a third gradually replaced it by a similar sliding movement, the atom so removed necessarily entering into combination with a fourth.

* Abstract of a Paper read before the British Association, Section B, Newcastle Meeting.

THE USE OF GLYCERIN IN PRESERVING SOLUTIONS OF SULPHURETTED HYDROGEN.

By ALFRED J. SHILTON, F.C.S.

A number of conflicting statements have been made as to the action of glycerin on a solution of sulphuretted hydrogen; I think it was Lepage who first recommended its use in the laboratory for this purpose, but it has since then been denied to have any preservative action whatever. Perhaps the following simple experiment will clear up the matter once for all:—

On November 6th I made up two white glass-stoppered bottles (*a*) and (*b*).

(*a*) Contained 50 c.c. saturated solution of sulphuretted hydrogen gas in water.

(*b*) Contained 50 c.c. of the same solution as in (*a*), but with 1 c.c. of glycerin in addition. The bottles were placed side by side on the laboratory shelf, and were left

until December 31st; they were then opened, and each of them found to smell strongly of the gas and to give a precipitate with lead acetate solution. They were re-closed, and not again examined until March 30th. When opened on that date the bottle (*a*) had entirely lost its odour, and gave no precipitate with a salt of lead, but the bottle (*b*), which contained the glycerin, had a strong odour, and gave a copious precipitate with lead acetate.

THE IODINE ABSORPTION OF ESSENTIAL OILS.

By R. A. CRIPPS, F.I.C.

Mr. Rowland Williams (Chemical News, vol. lx., p. 175) has drawn attention to the use of Hubl's iodine absorption test as applied to the examination of essential oils.

It is, however, somewhat unfortunate that Mr. Williams has apparently deviated from the lines laid down by Mr. R. H. Davies, whose paper on the same subject was published in the *Pharm. Journal*, [iii.], xix., p. 821; consequently his results differ widely from those obtained by Mr. Davies. The latter, in his paper, has shown that many essential oils act but slowly upon Hubl's reagent; it is therefore necessary to allow the digestion to be continued during a night. Mr. W. H. Snow has also shown the desirability of giving a longer time than two hours to the digestion; he finds that some oils require 40 hours, and even longer, for the completion of the reaction. This is, however, too long for practical use; it were better to adhere to Mr. Davies's plan of digesting during a night, but allowing a definite time, say eighteen hours, which is sufficiently long for the great majority of essential oils.

Temperature is another important factor in the determination of the iodine absorption of essential oils; at any rate, in those cases in which the reaction does not become completed in eighteen hours at the ordinary temperature, the difference between an ordinary summer and winter temperature would be sufficient to render the results untrustworthy. For the sake of comparison I append a Table of the results obtained by different observers with the most important oils.

I will not trespass further upon your space to make extended remarks upon the above Table; it is evident that the test is practically valueless unless performed under strictly concordant conditions, even then its indications will be of no value until a considerable number of samples of each essential oil have been reported upon.

Name of oil.	Barenthin.	Davies.	Snow.	Williams.
Almonds		None		
Aniseed	164·0	189·7	121 (40 hrs.)	185·9, 274·4
Bergamot	260·0	276·1	345 ,,	247·9, 283·7
Cajeput				70·85, 151·0
Caraway	265·0	*254·9	233 ,,	258·3, 463·2
Cassia		159·5		71·7, 75·1
Cedar				74·8, 78·5
Celery		*311·6		
Chamomile		*68·1, *72·1, 65·5		
Cinnamon	100·0	189·5		105, 128·1
Citron				320, 353·9, 359·66
Citronelle				186·3, 191·25
Clove (English)	270·0	349·5, 355·1, 362·5, 366·6	467 ,,	155·5, 179·8
Cubebs (English)		223·1, 226·0, 226·8		
Dill		*257·1		
Eucalyptus				61·7, 106·5, 110·6
Fennel	140·0	158·3		
Juniper	245·0	*337·3, 363·9†		236·1, 250·1, 273·5
Lavender (English)		265·5, 274·9, 273·9	286 ,,	230·4, 232·9, 248·6
,, (French)	170·0	262·7, 286·2, 294·5		198·6, 199·2, 237·2
,, (Spike)				287·9, 207·0
Lemon		328·3, 340·3, 345·3	343 ,,	320·16, 322·96
,,		348·9, 348·0, 345·6		
,,		355·1		
Nutmeg		*308·3, 321·5†		201·9, 206·25
Orange			362	341·7, 347·7
Pennyroyal		†188·9	152 ,,	85·9, 78·6
Peppermint (English)		49·6, 51·2, 57·7		36·85, 46·37
,, (American)		121·8, 132·2, 143·9	23, 84·7, 88·3 (6 hrs.)	71·7, 53·1
		81·9	24·5, 74·1, 73·6 (15 hrs.)	
			179, 109, 67, 71, 106, 105 (40 h.)	
,, (Jap.)		48·1, 43·5	64 (40 hrs.)	56·1, 37·1
Rosemary	185·0	†325		161·7, 142·4
Sandalwood (English)		226·6, 233·9		
Turpentine	300·0	377	397	

* English. † Foreign.

A SPECIFIC GRAVITY BOTTLE FOR USE IN TROPICAL CLIMATES.

By C. J. H. WARDEN,
Chemical Examiner to Government, Bengal.

The specific gravity bottle, with a capillary fore-stopper, though commonly used in temperate climates, cannot be used in Bengal, for the following reasons:—In my laboratory, Calcutta, for a greater part of the year the temperature is usually between 80° and 95° F., and the air highly charged with moisture. Under such conditions, when a specific gravity bottle is filled with liquid, cooled to 15·5° C., and the capillary fore-stopper inserted, the bottle cannot be immediately weighed, because, owing to the extreme humidity of the air, water is condensed on the surface of the bottle far too quickly to admit of even very rapid weighings, and by the time the temperature of

the liquid has reached that of the balance case it has necessarily expanded, and a large amount escaped through the capillary orifice in the stopper. In order to obviate this difficulty, 1884, I had ground on to the neck of the bottle a light glass cap, with a capillary orifice at the top, of sufficient capacity to hold 4 or 5 c.c. when using a 50 grm. bottle. The bottle is filled with the cooled liquid in the usual way, the capillary fore-stopper inserted, quickly wiped, and the glass cap fixed tightly on the neck. The bottle is then allowed to reach the temperature of the air, the expanded liquid forced out through the capillary orifice in the stopper being prevented from escaping by the cap, the capillary orifice in the top of the cap allowing the displaced air vent. Obviously it is very essential that the glass cap should be most accurately ground on to the neck of the bottle.

I ought, perhaps, to apologise for describing so simple an experiment, but, so far as I am aware, bottles modified on the plan I have detailed have not hitherto been procurable from instrument makers. Messrs. Edward Cetti, of Brooke Street, London, E.C., are now, however, prepared to supply capillary fore-stoppered specific gravity bottles with caps, for use in tropical climates.

Calcutt

AN IMPROVED METHOD FOR THE FORMATION OF REGULAR CRYSTALS.

By H. N. WARREN, Research Analyst.

For the formation of crystals, of a perfect and definite form, the method known as growing the same, aided by spontaneous evaporation, has, perhaps, ranked as one of the most successful. This, however, is, for the most part, considerably tedious, and, without a fair experience, often causes an experiment of long duration to terminate in the production of mal-formed specimens or of an exceedingly brittle structure. Thus, amongst the numerous crystallisable salts none are more distinguishable than the alums, both on account of their magnitude and their symmetrical appearance.

As an improved method of obtaining the same a concentrated solution of potash-alum was obtained by dissolving a pound of alum in about a litre of water, and placing the same in a bath maintained at a temperature of about 80° F. At the termination of an hour small but very perfect octahedrons were obtained, these were detached from their mother-liquor, selected, and placed aside for completion. The maternal solution was now cooled to 60° F., depositing a further quantity of agglomerated crystals, which were separated by decantation, and to the solution retaining the remainder of the alum were returned the selected crystals. The lower extremity of the vessel containing the same was next surrounded by a refrigerative mixture, composed of equal parts of potassic nitrate and ammonium chloride, in sufficient quantity to last for several hours, and placed in such a manner that the uppermost layer sustained a temperature of about 50° F., and containing a feeding tube, in which was inserted a further quantity of alum, and supplied at intervals, in order to replenish and sustain the strength of the solution. The small crystals, as obtained by the first operation, when subjected to this treatment, rapidly increase in size and shape; twin crystals, or small ones, which are apt to collect upon the sides, may be removed by the careful application of a smooth surface, of sufficient hardness, and washing with water. Chrome-alum thus treated yields most beautiful and perfect crystals. Not amongst the least beautiful may be mentioned those of potassium ferrocyanide, which appears of a transparency equal to that of glass.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

EXPERIMENTAL RESEARCHES IN THE REDUCTION OF THE DIFFICULTLY REDUCIBLE METALS.

By A. J. ROGERS.

(Concluded from p. 230).

The melting-point of the double chloride is less than 200° C., while that of pure Al is 700° C., and of cryolite nearly 1000° C., so the Al is perfectly fluid and readily coheres when reduced from cryolite. At the same time, the temperature is not sufficiently high to volatilise the Al. Cryolite, or other fluoride, has the disadvantage, as compared with the double chloride, of tending to flux the containing vessel, and greater care is necessary in the selection of materials for crucibles or crucible linings, and the temperature must be kept as low as other circumstances will permit. There is little difference in the transfer resistance in either class of salts. The addition of chlorides of the alkalies, or of the alkaline earths, permits electrolysis with a somewhat lower electrical potential. It is probable that there is more solution of the metal, and diffusion and re-union of the ions generally, in the electrolysis of the double fluoride than of the double chloride. I have repeatedly passed a current of 60 to 80 ampères through pure melted cryolite for several hours without obtaining more than a grm. or so of the metal. In those experiments an alumina-lined clay crucible was used, containing 25 to 30 pounds of the salt, with carbon cathode at the bottom of the crucible and a similar carbon anode passing in at the top. A tight-fitting cover prevented access of air from the top. Drawing the electrode farther apart increased the yield of metal from the same number of ampères. Mechanical agitation, or boiling, of the liquid would also tend to convey some of the Al through the molten mass, and thus bring it in contact with the liberated fluorine. Cryolite, when solid, has a higher specific gravity than Al, but when liquid the Al will sink to the bottom of it. It is doubtless true that with the temperature very high, the liberated Na from the cryolite does not reduce the Al, but passes off as a vapour at the top of the bath, or re-unites with the fluorine, and thus only a small amount of Al would be deposited at the cathode. I think it hardly probable that the reduced Al converts the Al_2F_6 of the cryolite to a lower fluoride.

It is probable that Al_2F_6, when pure, is not an electrolyte, as the resistance increases as other salts present decreases. Prof. W. Hampe gives experimented proof in the *Chemiker Zeitung*, August 3, 1887, that the pure chlorides, bromides, and iodides are not electrolytes. That has been my experience with carefully prepared pure Al_2Cl_6. I attempted to pass the current from a 30 cell Grove battery in series, using carbon electrodes a sixteenth of an inch apart, in Al_2Cl_6 without any deflection of the needle of a sensitive galvanoscope. The melting of the Al_2Cl_6 was made to take place, and the circuit closed, under paraffin, and also in glass vessels in which there was no access of air. On account of the great volatility of the salt an exit was allowed for the large amount of vapour passing off in the melting. It is still more improbable that the oxide of Al is an electrolyte, although it is regarded as such by Heroult, in U.S. patent, August, 1888. He passes the current through Al_2O_3, using copper as negative electrode on the bottom of a carbon crucible, and a carbon rod as positive electrode, and extending down from the top nearly or quite touching the copper. A powerful current fuses the Al_2O_3, which, at this high temperature, in presence of the carbon and copper, is reduced, and forms with the copper aluminium bronze. That there is no electrolysis I am convinced from the following experiments:—

I passed a current of 80 ampères for half an hour through Al contained in a carbon crucible having copper in the bottom. Some time after fusion took place, the current was broken, and a sensitive galvanometer showed

no deflection of the needle when put in the alumina current.

There seemed to be no electrolytic conduction, inasmuch as the current did not pass with 50 volts if the carbon electrode did not form at least a loose contact with the copper, or was not connected by particles of carbon, Further, the direction of the current made no perceptible difference with the amount of Al set free to unite with the copper to form bronze. I also used an alumina crucible, with copper and platinum electrodes passing through the crucible nearly horizontally, and forming loose contact in the centre of the mass of alumina. No alloy of copper was formed containing Al, and no polarisation could be observed, though the fusion was complete, and, of course, with it the copper and platinum.

What I desire more particularly to present in the present paper are the results of some experimental work performed during the past three years, in the electrolysis of mixed NaCl and cryolite, using molten negative electrodes and more especially lead.

Lead (Pb), tin (Sn), zinc (Zn), cadmium (Cd), antimony (Sb), and bismuth (Bi) were used. They all readily alloy with Na, and these alloys will give up the greater part of the Na when placed in melted cryolite, and alloys of these metals with Al will be formed or the Al set free.

A large portion of the Na (or K) can be recovered from these various alloys by distillation in an iron crucible. They can be heated to a higher temperature than pure Na, or K, in acid crucibles without the Na, or K, attacking the crucible. One part of Na added to 9 parts of Pb and melted under paraffin forms an alloy (NaPb probably), which still retains much of the appearance of the Pb, though harder and more brittle, and when placed in water acts very slowly upon it.

One part of the Na to 4·5 parts of Pb (Na_2Pb) gives a brittle, almost granular, alloy, having a blue-black colour, and acts quite rapidly upon water.

One part of Na to 2·25 parts of Pb (Na_4Pb), forms a dark blue iridescent alloy, quite compact, with a smooth cleavage, and acts very rapidly when thrown upon water.

One part of Na to 1·5/6 Pb is less homogeneous than the preceding alloys, and cuts with a knife like Na.

One part of Na melted with 14 parts of Sn, under paraffin, gives an alloy that is not homogeneous, which is of a blue-black colour on the top of the mass, and of a hard, metallic, some what brittle character on the bottom, forming two distinct alloys.

One part of Na to 6 parts of Sn, melted under paraffin, gives a more homogeneous alloy than the first, and of a darkish compact character, not very brittle.

One part of Na to 3 parts of Sn gives a homogeneous mass of blue-black colour, melting at a point just above the boiling-point of paraffin and considerably above that of pure Sn.

One part of Na to 1 part of Sn gives a granular alloy that melts at about the melting-point of Sn. When thrown upon the water the Na unites with considerable energy with the water.

One part of Na to 0·5 part of Sn gives an alloy that cuts like Na, and resembles it in appearance, and when thrown upon water the Na unites with so much energy that the liberated H ignites, and the black powder of Sn falls to the bottom.

In a future paper I shall hope to give some of the physical and chemical properties of these alloys with varying amounts of Na and K.

In the following will be found a few typical experiments incidentally illustrating the preparation of a few of these alloys by electrolysis, and especially the preparation of Al and its alloys. In a large portion of this work a 40 volt 90 ampère dynamo machine was employed, and Ayrton and Perry's instruments for measuring volts and ampères were used.

The following experiment illustrates the formation of Pb and Sn alloys.

Experiment 1.—A current averaging 72 ampères and 33 volts was passed through melted NaCl contained in two No. P Morgan crucibles, arranged in series, or two hours. Each crucible contained 30 pounds of the salt. In the bottom of the first crucible was placed 104 grms. of Sn, and of the second 470 grms. of Pb, each serving as cathode, connection being made through the bottom of the crucible. A carbon anode passed through the cover of the crucible and extended to within three inches of the molten metal cathode.

The crucible containing the Sn cathode was nearest the fire, and consequently hotter, and had an average potential difference across the electrodes of 12 volts, while that containing the Pb cathode was 21 volts. At the end of two hours the carbons were removed, the liquid allowed to cool, and crucibles broken open. The Pb alloy formed was of an iridescent shining bluish cast, and quickly dimmed on exposure to the air. It had a smooth cleavage and was very brittle. About 400 grms. of the pure alloy were removed, and the remainder, with adhering NaCl, put in water, and the Na estimated by standard acid solution.

When a piece of the alloy was thrown into water the action was very energetic, and when the alloy was exposed to the air it rapidly oxidised, and absorbed moisture from the air, and became very warm. The bottom of the crucible was protected from excessive heat, and the alloy produced no perceptible action upon it. The total amount of Na as sodium hydroxide was 165 grms., corresponding to 96 grms. of the metal Na. The theoretical amount of Na deposited in two hours with 72 ampères is about 122 grms. The tin alloy formed a solid mass of one-half inch in thickness, and 4·5 inches in diameter. It had a fibrous or striated character in a vertical direction nearly or quite as soft as pure Na, and when freshly cut resembled Na somewhat in appearance, having a steel-grey or ash colour. It easily ignited spontaneously in the air, and when thrown upon water the energy was so great that combustion of the liberated hydrogen took place. In these rich alloys the Pb and Sn were found at the bottom of the vessel of water, in a finely divided state, after the Na had entirely united with the water. There were about 90 grms. of Na alloyed with the Sn. Some of this alloy was preserved under paraffin for more than a year with only slight oxidation of the Na upon its surface. These alloys reduced Al from cryolite, or the chloride of Al, though the Na does not entirely leave the Pb, and considerable Na vapour passes off from the melted cryolite.

Experiment 2.—This experiment was repeated under the same conditions, using 2 pounds cryolite mixed with 36 of NaCl in each crucible. About the same amount of Pb and Sn alloy of Na was obtained, together with a considerable number of small globules of comparatively pure Al. I collected the globules formed on the surface of the Pb alloy, and, after re-melting, first under NaCl then in the air, a single globule was obtained, weighing 3·256 grms., and having a specific gravity of 2·71. Traces of Pb were present. The amount was decreased by re-melting in the air. Three buttons of an alloy of Al and Sn in the crucible containing the Sn cathode together weighed 4·46 grms., having a specific gravity of 4·69. This would indicate that the alloy contained about 45 per cent of Sn, and 55 per cent of Al, which would approach the formula Al_6Sn. There seemed to be little metallic Al present in the SnNa alloy. The liquid was agitated several times during the electrolysis with a carbon rod. The PbNa alloy contained some Al, which could be precipitated as hydroxide of Al from the aqueous solution of the alloy by neutralising with acid.

Experiment 3.—In another experiment I passed a current, having an average of 54 ampères and 10 volts, for 5·5 hours, through a mixture of 1 part cryolite and 5 parts NaCl in a single crucible having 370 grms. Pb as cathode. Upon opening the crucible 25 grms. of Al in globules, quite free from Pb and Na, were upon the top of the PbNa alloy. This Al had a specific gravity of 2·67, and contained some iron and silicon from the cryolite and

crucible. The very brilliant PbNa alloy contained some Al which could not be extracted by heating in air, but could be obtained by heating under NaCl.

The amount of Na present was 120 grms.; not much less than the theoretical amount. This was produced by a current of 54 ampères and 10 volts, working 5·5 hours, which is equivalent to one electrical horse-power for four hours.

Experiment 4.—Another experiment with two crucibles having 500 grms. of Pb as cathode, and with a current of 80 ampères, for four hours, and salt 1 to 5 of cryolite and NaCl, gave in one crucible 4 grms. of Al in small globules. and in the other no Al, with but a trace in the PbNa alloy formed. It is thus seen that the Pb must acquire a certain richness of Na before the Na will part from it to reduce the Al from cryolite diluted with NaCl.

Experiment 5. — In another experiment with two crucibles I used 90 grms. Pb in one, and 12 grms. in the other, with 1 to 5 of the salts cryolite and NaCl. Current was acting for four hours, having 80 ampères and 20 volts in both crucibles. The crucible having 90 grms. of Pb had an average of only 6·5 volts, being hotter than the other, and contained 15 grms. of free Al, besides the PbNa alloy, while no free Al was found in the other crucible, which was continuously at a lower temperature during the electrolysis. Re-melting the PbNa alloy of the two crucibles with cryolite gave 75 grms. of Al containing some Pb, Si, and Fe, and had a specific gravity of 2·89.

Experiment 6.—In another experiment 75 ampères were passed through two crucibles in series, with 6 volts in one crucible and 15 in the other, acting 6·5 hours; 400 grms. Pb were used in each crucible. A few globules of Al were found in the 6 volt crucible, but none in the other. The most of the alloy was re-melted in cryolite, and gave 155 grms. of Al. Theory would give about 325 grms. The crucible having the greater voltage gave no more Al than the other, and the electrical energy could have been reduced one-half with the same result. The energy actually consumed was equivalent to one electrical horse-power working twelve hours, which, as above stated, might have been reduced to one-half that amount.

Experiment 7.—In another experiment, running through two crucibles for seven hours, with 75 ampères and about 5 volts in each crucible, I obtained from 500 grms. of Pb for cathode 105 grms. of a highly siliceous Al from one crucible and 75 from the other. The heat was very high in both crucibles, and the Na had eaten more than half way through the clay crucible.

Experiment 8.—Passed 80 ampères with 24 volts through four crucibles, in series, for six hours, using 1 of cryolite to 3 of NaCl, with 450 grms. Pb in each crucible. Crucibles were lined from the bottom half way up the side with alumina, and the heat was regular and not too high, and the crucible scarcely acted upon by the cryolite or Na or Al. When the dynamo was thrown out of circuit at the close of the work, there was a potential difference of 12·25 volts across the four crucibles in series for several minutes, making 3+ for each crucible.

Exner gives the potential of NaCl with carbon electrodes at about 2·2 volts. 250 grms. of quite pure Al were obtained, with a large amount of Na in the re-melting with cryolite. There was then actually obtained, besides all losses, in round numbers, 1 pound of Al to the electrical horse-power per day of twenty-four hours.

Experiment 9.—Passed current of 73 ampères, on an average for four hours, through four crucibles in series, with 5 volts in each of three crucibles, and 20 in the fourth crucible. Obtained about the same amount in each crucible, 50 grms., or about 200 in the four crucibles; 54 pounds of NaCl and 18 pounds of cryolite were used in the four crucibles. The crucibles were lined half way up from the bottom with alumina. The fourth crucible could have been worked by 5 volts by bringing the electrodes nearer together, or raising the temperature of the electrolyte.

The preceding are a few of a large number of experiments illustrating the preparation of Al and its alloys by electrolysis. From my work thus far I cannot give complete experimental data as to the practical yield of Al that can be obtained from a given quantity of cryolite, or other fluoride or chloride. Probably 8 to 10 per cent can be obtained from cryolite, where the theoretical yield is 12·85 per cent.

I have generally used carbon rods 2·25 inches in diameter as anodes. A sample of 0·708 grm. of this carbon, heated on platinum foil for four hours in the air, gave 0·003 grm. of reddish residue, insoluble in common acids. These rods, if kept from action of the air during electrolysis, would last for forty-eight hours without much erosion. Carbon plates and cylinders were used, but the solid rods proved better in practice.

It is stated in Watts's "Chemical Dictionary," under Fluorine, that Cl displaces the F in any fluoride. In the preceding experiments Cl was certainly given off in large amount. The gases from the crucibles were allowed, however, to pass up the chimney, and I have as yet had no opportunity of analysing them. I have used various basic linings for my clay crucibles, but alumina has thus far succeeded best. I tried some "shrunk" magnesia from basic steel works, but it contained so much iron that I could not use it. If free from Fe it might answer very well. Lime can not be used, as it fluxes very readily.

Analyses of various samples of Al, obtained by the use of a Pb cathode, showed Al varying in purity from 75 to 99 per cent. Silica was present in quantity varying from 25 per cent to a trace, and iron varying from 5 per cent to a trace, and admixed Pb varying from 3 per cent to 0. There was but little loss in the quantity of Pb, and it could be repeatedly used.

The very low voltage and large quantity of metal obtained for a given number of ampères would seem to promise much for this method of extracting Al. More than a pound of Al to the electrical horse-power for twenty-four hours has been actually obtained, and, undoubtedly, continued experience will give a much better result.

The best results, and in fact the only quantitative results that have yet been published, so far as I am aware, for the separation of Al by electrolysis, are reported by Dr. John Hopkinson of the Kleiner process, where 3 grms. were produced to the electrical horse-power per hour, which would be about one-sixth of a pound in twenty-four hours.

Dr. Hopkinson reports that they used 60 volts to keep the cryolite in a state of fusion and electrolyse the salt. I cannot at present refer to details of work on the obtaining of pure salts of Al as electrolytes, and of durable crucibles, free from Fe and Si, besides mechanical arrangements and devices.

THE PRECIPITATION OF MAGNESIA.

By L. BLUM.

Dr. Mohr recommends to precipitate magnesia, not with sodium phosphate (disodium hydrophosphate), but with sodium-ammonium phosphate. As evidence he communicates a number of experiments from which it would appear that the precipitation with the latter salt is more rapid and more complete. By precipitating more and more dilute solutions of magnesia mixture he arrived at a point where sodium phosphate no longer gave a precipitate, whilst sodium-ammonium phosphate still occasioned precipitation.

Mohr overlooked, however, a circumstance of great importance in analytical practice, *i.e.*, that the precipitates obtained with the latter phosphate settle with extreme difficulty, whilst in precipitation with sodium phosphate, if the prescribed conditions are observed, the

deposition and complete separation of the magnesian precipitate is effected in a few hours, so that Fresenius prescribes only twelve hours' settlement before filtration.

The author, in the analysis of iron ores and furnace-slags, has been much engaged with determinations of magnesia, in which the quantity found never exceeds four per cent. In these cases small quantities of magnesium-ammonium phosphate have to be thrown down in presence of considerable proportions of ammonium chloride and oxalate and free ammonia, as the precipitation is always effected after the removal of the lime.

If sodium-ammonium phosphate is used the liquid becomes at once very turbid. The precipitate is of an extremely fine crystalline texture, whereby the settling is uncommonly delayed. In general the supernatant liquid does not become perfectly clear, even in four days. If we filter without previous settling the liquid runs through turbid, even with a double filter. With larger quantities of magnesia, if, *e.g.*, 1 c.c. of magnesium-mixture is precipitated, this inconvenience (as Mohr previously observed) does not occur. The precipitation and the subsidence of the precipitate ensue almost instantaneously, and we may filter immediately without the liquid running through turbid.

If we use sodium phosphate for throwing down the magnesia the precipitation is not so rapid, and at the outset not so decided. The precipitate when once formed settles well in a few hours, and the filtration presents no difficulties. The precipitation is as complete as with sodium-ammonium phosphate, as is proved by the following experiment, which has been often repeated:—

Two portions of magnesia were thrown down, A with sodium phosphate and B with sodium-ammonium phosphate. The filtrates from magnesium-ammonium phosphate were mixed, A with sodium-ammonium phosphate and B with sodium phosphate. Both portions, after standing for some days, gave a trifling deposit, the origin of which is explained by a phenomenon observed by W. Hintz, that an excess of the precipitant diminishes the solubility of ammonium-magnesium phosphate in water containing ammonium chloride and ammonia.

For the precipitation of small proportions of magnesia as they commonly occur in ores and furnace products, sodium phosphate is, therefore, contrary to the view of Mohr, preferable to sodium-ammonium phosphate. For the qualitative detection of magnesia, on the other hand, sodium-ammonium phosphate is preferable, of course only in such cases where the detection of alkalies in the same liquid is excluded.—*Zeitschrift f. Anal. Chemie*, Vol. xxviii., Part 4, pp. 452—454.

University College, Gower Street.—A series of evening discourses on Selected Branches of Applied Chemistry, illustrated by experiments and diagrams, &c., will be delivered in the Chemical Theatre on Wednesday evenings, at 8, commencing on Wednesday, December 11. They will be opened with a short address by Sir Lowthian Bell, Bart., F.R.S., D.C.L., President of the Society of Chemical Industry, &c., &c., who will take the chair on the occasion of Dr. Wright's first discourse on Dec. 11. Course I.: Dr. C. R. Alder Wright, F.R.S. (December 11 and 18), on Scientific Investigation as applied to the Manufacture of Iron and Steel. Course II.: Dr. Ferdinand Hurter, Vice-President of the Society of Chemical Industry (January 15, 22, and 29), (1) On Fuel; (2 and 3) The Sulphuric Acid Chamber and Process, with Modern Theories of the Chamber Process. Course III.: Dr. Adolf Liebmann (February 5), on the Applications of Organic Chemistry in some of the more recent Developments of the Coal-tar Industry of Dyeing and of Therapeutics. Course IV.: Watson Smith, F.C.S., F.I.C., Lecturer in Applied Chemistry in University College (February 12 and 19), on the Applications of Chemistry to Domestic Economy and Sanitation

RELATIONS BETWEEN THE COMPOSITION AND THE ABSORPTION-SPECTRUM OF ORGANIC COMPOUNDS.

By MAX. ALTHAUSSE and GERHARD KRÜSS.

By careful measurements of the absorption-spectra of a large number of organic compounds which have known relations to each other one of the writers has repeatedly investigated the connection between the spectrum and the composition of organic bodies.

The experiments were summarised about a year ago in a communication to the *Zeitschrift fur Physikalische Chemie* (ii., p. 312). It was found that almost without exception the introduction of methyl, ethyl, oxymethyl—*i.e.*, those groups which increase the proportion of carbon in a compound—and also of the carboxyl-group, there is produced a displacement of all the absorption-bands of a spectrum towards the red. On the other hand, a displacement of the bands towards the blue end of the spectrum ensues when an atom of hydrogen in an organic compound is substituted by a nitro- or amido-group.

The accuracy of these propositions has been repeatedly confirmed by an examination of substituted thionines, a selection of which has been placed at the disposal of the authors by Herr A. Bernthsen. They give an account of this research, as well as of some experiments which show that the introduction of hydrogen into an organic colouring-matter has a considerable, and, as it appears, a regular influence upon its spectrum.

The absorption-spectra of the following bodies were compared:—

1. *Thionine and Dimethylthionine Hydrochlorates.*—Each of these has, in its spectrum, three absorption-bands. The one situate nearest the refrangible end of the spectrum disappears on the dilution of the liquid just when the two other bands become separately visible and measurable. The maximum darkness of the several bands were measured in ten-millionths of the wave-length (Angström), as follows:—

	1st band.	2nd band.	3rd band.
Thionine hydrochlorate ..	606·5	587·4	563·7
Dimethylthionine hydrochlorate	616·8	595·1	576·0

The wave-lengths of the thionine bands increased on the introduction of methyl, the absorptions being displaced toward the red.

2. *Symmetrical Dimethylthionine and Symmetrical Diethylthionine Hydrochlorates.*—These compounds display bands similar to the above, and the measurements of the wave-lengths were as follows:—

	1st band.	2nd band.	3rd band.
Dimethyl compound ..	616·8	595·1	576·0
Diethyl ,, ...	621·1	604·2	578·0

An addition of CH_2 here also displaces the absorption-bands towards the red.

3. *Tetramethylindiamine- and Tetraethylindiamine-sulphides.*—The alkylised indamine-sulphides have also spectra with three absorption-bands, but the least refrangible band lies so close to the red extremity of the visible spectrum that its wave-length could not be measured. The maximum darkness of the other bands were determined.

	1st band.	2nd band.
Tetramethylindiamine sulphide ..	651·8	596·3
Tetraethylindiamine ,, ..	656·5	604·2

4. *Thionoline and Methylen Violet.*—The alcoholic solutions of both these bodies, even when rather strongly diluted, transmit little but red light. After a considerable addition of alcohol the blue of the spectrum becomes clear, and two bands are visible, possessing the following wave-lengths:—

	1st band.	2nd band.
Thionoline	575·2	550·7
Methylen violet	597·4	558·4

5. *Dimethyldiethylthionine Chloride and Tetraethylthionin Chloride.*—The two main bands of the thionine spectrum become visible on the strong dilution of the solutions of these compounds, and their maximum intensities have the following wave-lengths :—

	1st band.	2nd band.
Dimethyldiethylthionine chloride ..	655·2	605·4
Tetraethylthionine ,, ..	658·6	606·5

Here also an increase of the carbon of a compound displaces the absorptions towards the less refrangible end of the spectrum.

From the measurements of the thionine spectra it appears indifferent whether we study the spectrum of a base by observing its hydrochlorate, hydriodate, or any other salt. The bands peculiar to the base lie at the same part of the spectrum.

The Influence of the Introduction of Hydrogen upon the Absorption-spectrum of a Compound.

Hitherto nothing has been known as to the influence, if any, of the introduction of hydrogen into a compound upon the absorptions in its spectrum.

It seemed that this question might be partly solved by a careful spectroscopic measurement of the tetra-hydrated amine bases. Combinations such as diazobenzol chloride + α-naphthylamine and diazobenzol chloride + tetrahydro-α-naphthylamine were compared. The spectra of these and other bodies showed no even approximately measurable absorption-bands, but all these compounds have a sharp and rapidly measurable boundary of the absorption, which darkens the more refrangible end of their spectra. In order to recognise the influence of the introduction of hydrogen upon the position of the absorptions, this boundary was determined in the spectra of the solutions. The concentrations of these solutions were selected so that the number of grms. of the two substances to be compared were to each other as the molecular weights of these bodies. Thus, equal volumes of the solutions to be compared contained an equal number of mols., and on examining equal strata of these solutions the light had to pass an equal number of mols. of the compounds, hydrogenised or not hydrogenised. The position of the boundary of the absorption gives, thus, direct evidence on the influence of hydrogen upon the positions of the absorptions. From the measurements carried out it appears that an addition of hydrogen to an organic colouring-matter displaces the absorptions in its spectrum towards the blue.

Generally speaking the relations between the composition and the absorption-spectrum of a compound are identical with those between the colour and the composition of any substance; for the colour is the result of the light not absorbed by the compound. If a colouring-matter is examined by means of the spectroscope in such a manner that we measure accurately what kinds of light are transmitted by the technical solutions of the colouring-matter and what are lost by absorption, we can, in virtue of the laws above indicated, predict with tolerable accuracy what will be the colour of a substitution-derivative of the primary compound. If, *e.g.*, such compound has, in its spectrum, a band which absorbs the blue, then, by the introduction of methyl or ethyl, a body is obtained in the colour of which there comes into play more blue and less green. If the primary colour has an absorption-band in the red its colour will become redder by ethylation because the band will be displaced towards the ultra-red. The decision what will be the influence of the substitution of a colouring-matter by different groups will, according to the above results, be trustworthy only if the absorption-spectrum of the original colour has been previously studied. Such applications of the spectroscope will certainly, in many cases, prove of use in chromo-technics.—*Berichte der Deutsch. Chem. Gesellschaft*, Vol. xxii., p. 2065.

THE MANUFACTURE OF THE ALLOYS OF ALUMINIUM IN THE ELECTRIC FURNACE.*

By JOHN H. J. DAGGER, F.I.C., F.C.S.

(Concluded fom p. 227).

ALUMINIUM brass is another valuable alloy made by combining aluminium bronze with zinc in different proportions. It is a close-grained, homogeneous, and tough metal. The torpedo shell before you is cast from this metal (the No. 2 grade).

Aluminium brass.	Tensile strength in castings.	Elongation.
No. 1 ..	23—27 tons per sq. inch.	10—14 p.c.
,, 2 ..	30—34 tons.	6—11 ,,

This allloy forges hot, and its special casting properties, its resistance to corrosion, its low specific gravity, render it valuable as a material for ship's propellers, stern, and rudder frames, pump-plungers and rods, valves, wheels, and pinions, and for hydraulic and engineering work generally.

A number of tests were made by order of the navy department of the United States of aluminium bronze and brass, as compared with United States gun bronze, with favourable results.

A blade could be made of it at least one-third thinner than cast-iron or any other bronze blade, and would be correspondingly lighter.

For cartridge shells these alloys cannot be equalled; their strength would enable a thinner and lighter shell to be used, with the advantage of not being corroded by the contained explosive. The use of aluminium bronze as a material for cannon was the subject of a paper read before the United States Naval Institute in 1887. As early as 1859 a mountain gun of this metal was cast and tested by the Committee of Artillery of France, with very favourable results, the high price of aluminium being then the only thing prohibitive of its widespread use for guns.

The following are some results of mechanical tests of aluminium bronze and brass :—

COMPRESSION TESTS MADE AT WATERTOWN ARSENAL, U.S.A.

Original length.	Shortened to ins.	Original diameter.	Increased to ins.	Ultimate strength.	Ultimate strength.	Specimens (casting).
Ins.		Ins.			lbs. per sq. inch.	
2·00	1·705	0·798	0·865	80,200	160,400	"A" 1 bronze.
2·00	1·525	0·798	0·914	76,800	153,600	"B" 2 bronze.

TRANSVERSE STRENGTH.

Cross section of bar in sq. inches.	Length between supports. No. inches.	Breaking load in pounds.	Aluminium brass No. 2, cast in sand, tested at Milton.
1	12	8,100	

Deflection with 5000 lbs. load was but 0·04 inch, and permanent set 0·01 inch, showing remarkably high transverse elastic limit, great rigidity, and elastic resilience.

* Read before the British Association, Section B, Newcastle Meeting.

Tests of Aluminium Bronze and Brass.

United States Navy Department Tests.

	Mark or No.	Approximate composition. Cu.	Al.	Si.	Zn.	Sn.	Length between reference marks.	Diameter in ins.	Area in sq. ins.	Tensile strength.	Elastic limit.	Elongation per cent in 15 inches.	Reduction of area.	Diameter at fracture inches.	
							Inches.			lbs. per sq. inch.	lbs. per sq. inch.		Per cent.		
Aluminium bronze or brass.	1*c*	91·5	7·75	0·75			15	1·875	2·7612	60,700	18,000	23·200	30·7	1·56	Chill castings.
	7*c*	88·66	10·0	1·33			15	1·875	2·7612	66,000	27,000	3·800	7·8	1·80	
	9*c*	91·5	7·75	0·75			15	1·875	2·7612	67,600	24,000	13·00	21·62	1·66	
	10*c*	90·0	9·0	1·0			15	1·875	2·7612	72,830	33,000	2·40	5·78	1·82	
	11*c*	63·0	3·5	0·33	33·33		15	1·875	2·7612	82,200	60—73,000	2·33	9·88	1·78	
	11*d*	63·0	3·33	0·33	33·33		15	1·900	2·840	70,400	55,000	0·40	4·33	1·86	
	13*c*	92·0	7·5	0·5			15	1·875	2·7612	59,100	19,000	15·1	23·59	1·64	
	9*d*	91·5	7·75	0·75			15	1·900	2·840	53,000	19,000	6·2	15·50	1·75	Dry sand castings.
	10*d*	90·0	9·0	1·0			15	1·890	2·810	69,930	33,000	1·33	3·30	1·86	
	13*d*	92·0	7·5	0·5			15	1·930	2·930	46,550	17,000	7·80	19·19	1·73	
	1	88·0			2·0	10·0	15	1·875	2·7612	18,000	10,000	2·50	4·70	1·83	Green sand castings.
	2	88·0			2·0	10·0	15	1·875	2·7612	24,590	11,000	8·20	6·80	1·81	
	3	88·0			2·0	10·0	15	1·875	2·7612	22,500	11,000	5·80	10·89	1·77	
	4	88·0			2·0	10·0	15	1·880	2·7760	23,000	13,000	4·00	10·36	1·78	
	5	88·0			2·0	10·0	15	1·880	2·7760	20,570	13,000	2·33	6·30	1·82	
	6	88·0			2·0	10·0	15	1·880	2·7760	23,750	13,000	3·70	7·30	1·81	

Tests of Hardness of Large Bars.

Aluminium Bronze or Brass.

Mark.	Hardness of head.	Hardness of stem.
1*c*	9·39	13·85
7*c*	14·12	14·26
9*c*	11·18	13·59
11*c*	14·69	10·60
10*d*	17·08	16·07

Hardness of Navy Yard Bronze.

Mark.	Hardness of head.	Hardness of stem.
No. 1	3·33	3·33
„ 5	3·67	6·56

The Navy Yard bronze was furnished by the United States Government, and carefully cast at New York Navy Yard, under inspection of an officer detailed for that purpose.

William H. Harris,
Chief Engineer, U.S.N.

Tests made at Milton Works.

Description.	Original diameter.	Final diameter.	Original area.	Final area.	Original length.	Final length.	T S original section. Tons.	T S final section. Tons.	Elongation %.	Reduction of area.
Rolled No. 1 .. .. Brass	0·737	0·620	0·4266	0·3019	3·812	4·562	37·7	53·3	22	29·2%
Rolled No. 2 .. .. Brass	0·614	0·530	0·2960	0·2200	5·165	5·625	37·8	50·9	9·7	25·6%
Rolled "C" .. .. Bronze	0·731	0·400	0·4196	0·1256	6 ins.	8 ins.	34·3	114·6	33·3	70%
"Hercules" .. .. Metal rolled hot to 1⅛ in.	0·607	0·485	0·2893	0·1847	2·56	3·47	34·0	53·6	35	36%
"A" bronze .. .. No. 2 brass	0·599	—	0·278	—	2·46	—	44·5	—	5·7%	10%
Rolled hot from 3 sq. in. pillar to 1⅛ in., and cold to 1 in.	0·570	—	—	—	2·40	—	39·0 88,000 lbs.	—	12·5%	17·6%

Tests made to determine Effects of Temperature.

"A" aluminium bronze.	Diameter.	Length.	Tensile strength.	Elongation.
Cast in sand.. ..	0·330	1	116,000	5 not broken.
Duplicate	0·330	1	108,000	4 „ „
Same bar heated to 450° Fahr... ..	0·330	1	108,000	1 „ „
Cooled to temperature of room ..	0·330	1	109,000	„ „
Heated to 450° Fahr., or possibly somewhat higher temperature ..	0·330	1	86,000	5 bar broke.

Showing that this bronze retains its strength through a range of temperature. Aluminium brass No. 2 subject to like test broke at 29,000 and 35 per cent elongation, with very great contraction of area. When cold, the same bar resisted 85,000 pounds without rupture.

Aluminium Alloys.

Shrinkage per inch in 12 inches.

Aluminium Bronze.

	Dry sand.	Green sand.
A 1	1/11	2/11"
A 2	—	1/8"
A 3	8/44"	9/44"
C 2	—	1/4"

Aluminium Brass.

	Dry sand.	Green sand.
No. 1	$\frac{1}{8}$"	—
No. 2	$\frac{3}{22}$"	$\frac{3}{22}$"

Aluminium Hercules.

	Dry sand.	Green sand.
No. 3	$\frac{3}{44}$"	$\frac{3}{16}$"
No. 4	$\frac{3}{44}$"	—

Aluminium Bearing Metal.

	Dry sand.	Green sand.
No. 1	—	$\frac{9}{64}$"
No. 3	—	$\frac{11}{64}$"
Silicon	—	$\frac{1}{8}$"

Ferro-aluminium.—The alloys of aluminium and iron have long been known. They are referred to by Faraday, who found 0·013 per cent to 0·69 per cent aluminium in "wootz" steel. Rogers, in an article in the *Moniteur Industriel*, No. 2379, 1859, says a small per cent of aluminium makes steel hard, strong, and brittle; a larger quantity makes it very dense, without impairing its peculiar polish or detracting from its qualities.

The influence of aluminium in small quantity on cast iron is very marked, and was last year the subject of an interesting paper by Mr. W. J. Keep in conjunction with Prof. Mabery and L. D. Vorce, of the Case School of Applied Science, Cleveland, Ohio, U.S.A., read before the American Association for the Advancement of Science, August, 1888.

Two bases were used—one a white iron, with composition Si 0·186, P 0·263, S 0·0307, Mn 0·092; the other grey Swedish iron, marked F.L.M. with Si 1·249, P 0·084, Si 0·04, Mn 0·187. The ferro-aluminium used was made by the Cowles process, and contained Si 3·86, Al 11·42 per cent. Each based was experimented upon separately, and at the same time a series of blank trials were made, the metals in the two series being subjected to exactly the same conditions.

The following results were obtained:—

1st. *Solidity of Castings and Prevention of Blow Holes.*—The aluminium castings were of a slightly finer grain and of increased solidity, with 0·1 per cent Al present. The resistance to dead weight was increased about 44 per cent, and to impact 6 per cent.

2nd. *Does the Aluminium Remain in the Iron after Remelting?*—The white base, after the addition of 0·25 per cent of aluminium, was re-melted six times, fresh quantities of the white base being added each time. That the aluminium remains in and improves the iron is shown by the superior and stronger castings obtained in this series, even after the percentage of aluminium had become very low, than in those cases where no aluminium was added.

3rd. *The Effect of Aluminium on the Grain.*—Aluminium seems to enable iron to hold in solution all its carbon until just upon the point of solidification, when it is precipitated in a finely graphitic form. The advantage of this is the uniformity of the mass and the absence of pockets of graphite, which are generally produced when ordinary grey iron has been cooled slowly. Hence the homogeneity and greated strength of the aluminium castings. The rapidity of cooling makes little or no difference, as the release of the carbon seems to be instantaneous, and only at the moment of crystallisation. A very little aluminium is sufficient to precipitate graphite from white iron, 0·25 per cent rendering it perceptibly darker in colour, 0·5 per cent more so, whilst 0·75 per cent renders it quite grey with no signs of white. With increasing amounts up to 4 per cent, the maximum in all these experiments, the effect is the same, the castings becoming softer and greyer as the amount of aluminium increases. The presence of much silicon does not alter the matter. The grain being the same also in thin, and rapidly cooled, as in thick castings.

4th. Aluminium castings are not affected by chilling; graphite is liberated whether the casting is cooled rapidly or slowly, with the result that the grain is uniform, and there is no chill.

5th. When sufficient aluminium is present to liberate the graphite, a coating is formed on the casting which resists the sand and the heat, and prevents the iron burning the sand into itself.

6th. The fineness of the grain causes them to be more easily cut than cast-iron of coarser grain.

7th. The presence of aluminium increases the strength to sustain a constant load, but the strength does not increase uniformly with the percentage of aluminium.

8th. The increase in strength is much greater and more marked than in the preceding. Above a certain percentage the strength diminishes, due to larger amount of graphite liberated.

9th. Elasticity is improved.

10th. The fineness and compactness of iron containing aluminium gives less permanent set than iron equally as soft when that softness is produced by silicon.

11th. The shrinkage is slightly increased with a small quantity of aluminium, due probably to the elimination of blow holes; but with 0·75 per cent, and more, it is much decreased, especially in case of wrought-iron.

12. In case of the white iron fluidity is much increased—with grey base containing much silicon it is not so clear, though it is believed the fluidity is increased.

The fact that aluminium lowers the melting-point of iron is utilised in the Mitis castings, the invention of Mr. Peter Ostberg, of Stockholm. In making Mitis castings a very small quantity of aluminium, about 0·050 per cent Al in form of 7 or 8 per cent ferro-aluminium, is added to the charge (about 60 lbs.) of wrought-iron in the crucible the moment this has been melted. The fusing-point is at once lowered about 500°, and the charge becomes very fluid and can be cast in the finest moulds. The great difference between its temperature and its fusing-point gives all the time necessary for its manipulation without danger of its solidifying.

The tensile strength of Mitis castings may be as high as 27 tons per sq. inch, with an elongation of 20 per cent.

Another alloy made in the electric furnace is silicon bronze, which, owing to its great strength and tenacity, its resistance to corrosion, combined with high electrical conductivity, is perhaps the best metal extant for electric light, telephone, and telegraph wires.

In conclusion, may I direct your attention to the test bars, castings, and specimens of aluminium alloys made by the Cowles process, kindly lent for this paper by the Cowles Syndicate Co., Limited.

Specimens of Aluminium Alloys Made by Cowles Process.

Exhibited in connection with Paper read before B Section, British Association.

No. 1. Aluminium bronze cylinder (Torpedo shell), 2 feet long, 14 inches diameter, cast in sand with core; outside finely polished, inside rough.

Test bars taken from same pouring gave—

Tensile strength, 105,000 lbs. per sq. inch (46·87 tons).

Elongation, 6 per cent.

No. 2 Cylinder, same as above, made from aluminium brass "No. 2" (one-third zinc) (33·3 per cent).

Tensile strength, 90,000 lbs. per sq. inch (40·17 tons).

Elastic limit, 66,000 lbs. per sq. inch (29·46 tons).

Elongation, 6 per cent.

No. 3. Piece of calico-printing cylinder, 6 inches diameter and about 1 foot long, cast by Messrs. Bolton and Sons, Oakamoor Mills, Cheadle, Staffordshire, in the same manner as they cast their copper cylinders.

No. 4. Dynamo hub of aluminium brass, No. 2.
This metal has a tensile strength of 93,000 lbs. to the sq. inch, and 5 per cent elongation.
The German silver that has heretofore been used in the Brush hubs has but 44,000 lbs. tensile strength and 24 per cent elongation, and costs much more than this brass.

No. 5. Billet of 10 per cent aluminium bronze, cast in chill; one entire side polished to show perfect casting, colour, &c.

No. 6. Lathe turnings of aluminium bronze, showing no signs of oxidation after three years' exposure to the atmosphere.

No. 7. Aluminium "pig" casting (80 per cent aluminium), produced directly by heat of electric furnace. Reduction of oxide of aluminium by carbon (believed to be the first reduction by carbon of this oxide).

No. 8. North Metropolitan (London) Tramway Co.'s "car-bearing" of ordinary gun metal after a year's wear, and originally of same dimensions as No. 9.

No. 9. Same Co.'s car-bearing made from Cowles' aluminium bearing metal after a year's running on same route as No. 8, no wear being perceptible.

No. 10. Aluminium bronze bar, one end hammered hot, other end twisted cold.

No. 11. 5 per cent aluminium bronze bar, bending test, bent cold.

No. 12. 11 per cent aluminium bronze rolled sheet, test spring by bending.

No. 13. 5 per cent aluminium bronze rolled bar, tested at Phœnix Works, Ruhrort, Germany.
Tensile strength, 82,880 lbs. to the square inch (37 tons).
Elongation, 60 per cent.

No. 14. 5 per cent aluminium bronze cup, drawn cold from a 9 inch disc.

No. 15. Sample of silicon copper product run direct from furnace; silicon = 15·08 per cent.

No. 16. Bar of basic Siemens steel, tested at Phœnix Works, Ruhrort, Germany, showing bending and fracture.

No. 17. Bar of 10 per cent Cowles aluminium bronze, tested at Phœnix Works, Ruhrort, Germany, showing bending and fracture.

No. 18. One inch round bar of aluminium bronze.

No. 19. Two inch square bar of aluminium.

No. 20. Propeller blade of No. 2 aluminium brass.

No. 21. Ores, slags, fragments of carbon from the electric furnace.

No. 22. Drawings and views of the electric furnace, engine, dynamo.

No. 23. Photographs of the Cowles Aluminium Works, Milton, Staffordshire.

NOTICES OF BOOKS.

Coloured Analytical Tables showing the Behaviour of the More Common Metals and Acids with the Ordinary Reagents, with Special Reference to the Colour of the Various Oxides, Salts, Precipitates, Flames, Borax-beads, and Blowpipe Reactions. A Class-Book for Students in Hospitals, Colleges, and Schools. By H. Wilson Hake, Ph.D., F.I.C., F.C.S. London: G. Philip and Son.

The novelty of this work lies in the coloured illustrations. In the general table we find figured a portion of a small test-tube as containing a portion of a precipitate coloured as nearly as possible to the reality. This direct appeal to the eye will very probably help the student who has seen the experimental production of the precipitate to remember its appearance better than would a mere verbal description. The same system is followed as far as possible throughout the work.

As part and parcel of the necessary reaction against verbalism this little book has its merits.

Manures and their Uses. A Handbook for Farmers and Students. By A. B. Griffiths, Ph.D., F.R.S.E., F.C.S. London: G. Bell and Sons.

This work belongs to the valuable "Agricultural Series" now in course of issue by the publishers. It reminds us in many respects of the author's "Treatise on Manures," but it contains several improvements, and it is addressed more especially to the former. The author commences with an account of the rise and development of British agriculture, showing its alternating stages of prosperity and depression. It seems to us, in these days, strange to read of wheat being, in the Roman epoch, systematically exported from Britain to Germany and Gaul. At the same time our island supplied the Roman Empire with horses, cattle, cheese, and with chalk, lime, and marl for use as manures. In the thirteenth and fourteenth centuries it appears that the outside yield of wheat per acre was only 10 bushels.

The first crude outline of an agricultural chemistry seems to be due to Sir H. Platt in 1594. Bone-dust was first used by Colonel St. Leger on his farm near Doncaster in 1765, but it was not generally adopted for seventy years later.

The author cannot accept the doctrine of M. Ville that no soil needs any other addition save nitrogen, potash, lime and phosphoric acid, and insists upon the necessity of supplying what may be called the minor elements of plant-food in an available form. He agrees, however, substantially with M. Ville in holding that chemical analysis alone is no adequate clue to the requirements of a soil. Potash and phosphoric acid may be present in fair quantity, but if they are in a condition insoluble in water and in the acid secretions of the roots of plants the land will prove barren. The eight laws laid down on p. 20 as regulating the productiveness of a soil strike us as being eminently judicious. The last of them, we fear, too often escapes the attention of agriculturists. It is this:—"The manure produced in the course of husbandry is *not* sufficient to permanently maintain the fertility of a farm; it lacks the constituents that are annually exported in the shape of grain, hay, milk, and live-stock."

The table given on p. 24 arranges manure under the three heads of organic, artificial, and special. We can scarcely accept this classification, since there figure under the second head lime, gypsum, salt, silica, &c., which cannot be called "artificial." The table given on the opposite page, where manures are grouped according to the constituent which they supply to the soil, is preferable. Dr. Griffiths endorses the conclusion of M. Ville, that "the farmer who uses nothing but farmyard manure exhausts his land."

The action of certain microbia in inducing putrefactions and nitrification in manure heaps is here brought into the necessary prominence.

A temperature of 150° F. is fixed as the maximum permissible, and the use of a solution of ferrous sulphate is recommended for preventing the escape of ammonium carbonate. He has ascertained experimentally that peat-litter yields a better manure than straw-litter. A very serious defect of farmyard manure which, we think, has escaped the notice of M. Ville, is that it is "a medium in which fungoid diseases, such as the potato-disease, wheat-mildew, &c., are capable of hibernating for months without losing their vitality." Dr. Griffiths adds that "the wise farmer will never use farmyard manure obtained from turnip-fed cattle for turnip-crops."

Irrigation, the author thinks, should be practised only upon porous and well-drained soil. He speaks of the sewage farms in the neighbourhood of Paris as sending

their produce of vegetables to the Halles Centralles. The yield is certainly abundant, but the crops generally come later than those from non-irrigated soils, and hence command a lower price.

In the section on bone-manures the author quotes Liebig's terrible denunciation of England for denuding the world of bones and other mineral matter, and then letting the resulting excreta flow down into the sea. Of course, where we utilise sewage either by irrigation or by a precipitation process which yields manure, we no longer incur this censure. But where we still let it run down to the sea continuously or intermittently, or, worse still, where we precipitate the sewage and carry the deposit out to sea, we are guilty.

Want of space does not permit us to carry any further our examination of this valuable work, but we can conscientiously recommend it to the careful perusal of all persons interested in agriculture.

Notes on Qualitative Analysis; arranged for the Use of Students of the Rensselaer Polytechnic Institute. By W. P. Mason. Troy, New York: Nims and Knight.

The peculiarity in virtue of which Prof. Mason asserts that his work has a definite *raison d'être* is the frequent reference made to standard authorities, such as Fresenius, Watts's "Dictionary," Roscoe and Schorlemmer's great work, &c. It will doubtless be very useful for the student thus to fill in the necessarily meagre outline given in the text. But what of the many students who have not access to a well-stocked library? Would they not prefer a treatise which should at once supply all the information they require?

A commendable feature is that the student is recommended to use the spectroscope, *e.g.*, for the recognition of traces of potassium, and for distinguishing calcium from strontium.

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—Herr Wollheim, in his letter (Chemical News, vol. lx., p. 221), claims that the Amines sludge is so "permanently" sterilised that it will uot decompose even when placed upon the land. It is interesting to note with what this amount of work is done, and what are the results, so far as the manurial value of the sludge is concerned when it is done.

Herr Wollheim's last declaration is that he uses 6½ ounces per 1000 gallons, or 2·843 grains of herring-brine per gallon. Allowing it to be correct that herring-brine contains two-thirds of a percentage of trimethylamine, or a salt of that body equivalent to that quantity, then we should get 0·01876 of a grain per gallon. This, then, is the quantity, or its equivalent as "Aminol," which does the work. Allowing that this quantity can disinfect sewage, and even carry its powers with the sludge, so that the latter will not decompose when applied to land, then, as it appears to me, he has over-reached his prime object in putting it there; for he renders his sludge useless as a manure. The nitrogen of good sewage sludge is nearly all present as organic nitrogen, and therefore is not plant food until after decomposition or nitrification. "Permanent sludges" and undecomposable sludges, therefore, must remain on the land for ever as such, or, at all events, until the wonderful powers of "Aminol" have been exhausted.

It is passing strange that in order to liberate 0·01876 of a grain of trimethylamine such a large quantity of lime is needed.

In my opinion from 45 to 50 grains of lime per gallon are quite impracticable quantities when applied to large flows of sewage. Awaiting "certain investigations,"—I am, &c.,

Cyclops.

DETECTION OF ADULTERATION IN ESSENTIAL OILS.

To the Editor of the Chemical News.

Sir,—I was much interested in reading the article by Mr. Rowland Williams, on iodine absorption of essential oils, which appeared in the Chemical News, vol. lx., p. 175.

In connection with the examination of oil of peppermint for adulteration with oil of turpentine, I had occasion to employ the iodine absorption of the oils, and found it extremely useful. The work was somewhat extended, and determinations of the iodine absorption of a number of oils were made. The results were published in *The New Idea*, Detroit, Mich., U.S.A. (March, 1889, p. 17). The article on oil of peppermint was given in the same issue. These articles were repeated in the *Pharm. Journal and Trans.* (London) for July 6, 1889, p. 4, and June 29, 1889, p. 1056. The article on oil of peppermint was reprinted in the *Journal of Analytical Chemistry* (Easton, Pa., U.S.A.), for July. Closely following my results, Mr. R. H. Davies independently published in the *Pharm. Journal and Trans.* (London), April 13, 1889, p. 821, an exhaustive paper on this same subject of iodine absorption of essential oils. In searching after literature on the subject, Mr. Davies found that Mr. C. Barenthein, a pharmacist of Berlin, had given in the *Archiv de Pharm.*, October, 1886, determinations of the absorptions for eleven essential oils. So far as I know at present, the work of Mr. Barenthein is the first in this line.

The last six months have given us quite a literature on this subject, and all goes to show that "original work" is properly only the expression of prevailing tendencies. I have gone at some length into these references in the hope that they will be of interest to Mr. Williams and others, as they would be to me under the same conditions.—I am, &c.,

H. W. Snow.

Detroit, Mich., U.S.A.,
October 25, 1889.

MILK ANALYSIS.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lx., p. 233) Mr. W. Johnstone contends that *all* the fat can be extracted from a milk by a modified Wanklyn process. The higher results obtained by the paper-coil process, he says, are due to the increase of weight produced by oxidation. How then does he explain that similar higher fats are given by the (1) Soxhlet areometric process; (2) the lactrocrite; and (3) by the Schmid process, where there can (in the first, certainly), be no pretence of oxidation. It is singular that all these should agree with the calculated results, and with one another, in giving higher fat than the now generally discarded Wanklyn method.—I am, &c.,

Alf. W. Stokes, F.C.S., F.I.C.

Analytical Laboratory,
Vestry Hall, Paddington Green, W.
Nov. 11, 1889.

New Process for Preparing Oxamide and Oxamic Acid.—E. Matthieu-Plessy.—The author introduces ammonium oxalate into ammonium nitrate in fusion, and keeps the mass at 170° to 175° for four hours. On treating the mass with water he obtains oxamide and oxamic acid.—*Comptes Reudus*, Vol. cix., No. 17, Oct. 21, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 17, October 21, 1889.

Researches on the Relations which Exist between the Physical Characters of Plants and the Richness of the Soil in Fertilising Elements.—Georges Ville.—The characters of the plants which the author takes into consideration are the colour, the stature, and the entire weight. To limit the question he confines his studies to a single plant, hemp. These points are shown in an illustration which gives the comparative height of the plants, the weight of the crop, and the colours as seen in masses. The experiments were made with seven soils:—"Intense" manure (100 kilos. nitrogen), "complete" manure (75 kilos. nitrogen), manure without nitrogen, manure without phosphates, manure without potash, manure without lime, and soil without any manure. It must be remarked that M. Ville considers that plants require a supply of lime over and above that naturally existing in the soil, that present in combination with phosphoric acid, and that existing in the state of sulphate formed in the manufacture of superphosphate, and that he adds such further amount of lime in the form of gypsum. The hemp plants treated with "intense manure" were of the deepest green, reached the height of 1·53 metres, displayed the deepest green colour, and weighed 11·22 kilos. The plants with "complete manure" grew to 1·20 metres, were of a less deep colour, and weighed 11·15 kilos. Those without nitrogen reached only 0·61 metres were of a yellowish green, and weighed 4·74 kilos. Those without phosphates were 0·97 metre in height, were of a medium green, and weighed 8·22 kilos. Those without potash were only 0·40 metre in height, of a yellowish green, and weighed 5·22 kilos. Those without lime grew to 1·15 metres, were slightly paler than those without phosphate, and weighed 10·57 kilos. Lastly, the plants in unmanured soil were only 0·18 metre in height, were of a pale green colour, and weighed only 2·175 kilos. The author proposes to give in a future paper the determination of the proportions of chlorophyll and of carotine in plants differently manured.

The Simultaneous Synthesis of Water and Hydrochloric Acid.—P. Hautefeuille and J. Margottet.—In presence of chlorine or carbon monoxide the separation of the elements of water under the influence of heat determines the formation of gaseous mixtures, concerning the composition of which we have few accurate data. The authors have taken up the study of the decomposition of water under these conditions, and, before explaining the results reached when operating directly upon the vapour of water, they make known the composition of the mixtures formed in the synthesis of water in the presence of chloride, or in the synthesis of hydrochloric acid in the presence of oxygen. If the volume of chlorine in a gaseous mixture is greater than half the volume of the hydrogen in a gaseous mixture the number of equivalents of water and hydrochloric acid is always less than unity, and it decreases rapidly as the proportion of chlorine in the mixture increases. When the volume of the chlorine is double that of the hydrogen the water formed on the passage of the electric spark ceases to be appreciable. The weight of the chlorine remaining free is exactly half the weight of this gas introduced into the eudiometer. Every change in the proportion of chlorine added to the detonating mixture modifies the result. It is impossible to extend the mixtures containing chlorine; the law announced by Bunsen in consequence of his experiments on the combustion of mixtures of carbon monoxide, hydrogen, and oxygen, for the relation between the water and the hydrochloric acid formed in the combustion does not vary abruptly, but continuously on the progressive addition of chlorine to the detonating mixture. As regards the synthesis of hydrochloric acid in presence of oxygen, the authors find that the relation of the numbers of equivalents of water and hydrochloric acid formed by the combustion of mixtures obtained on adding oxygen to the elements of hydrochloric acid, is always less than unity, but it varies only within narrow limits on increasing the relation of the volumes of hydrogen from $\frac{1}{4}$ to 3.

On the Existence of Phosphonium Sulphate.—A. Besson.—If dry gaseous hydrogen phosphide is passed through pure sulphuric acid refrigerated down to −20° or 25° it is absorbed in quantity, and the liquid becomes syrupy. The product of the reaction is stable, and may be preserved if kept at some degrees below 0°. If the syrupy liquid is decanted out of the tube in which the reaction has taken place a solid white mass is found at the bottom, which seems to be crystalline phosphonium sulphate.

The Action of Ammoniacal Copper Sulphate upon Sorbite and Mannite.—M. Guignet.—A reply to the observations of MM. Vincent and Delachanal. The author has never denied that sorbite precipitates ammoniacal copper sulphate. On the contrary, he has affirmed "that mannite, dulcite, and probably the other isomers, produce at once blue precipitates in the solution of ammonium-copper sulphate."

The Part played by Ammonia in the Nutrition of the Higher Plants.—A. Müntz.—The author's experiments distinctly prove that the higher plants can directly absorb ammoniacal nitrogen by their roots, and that consequently the nitrification of ammoniacal manures is not a necessary condition for their utilisation.

Photometry with Nitrogen Iodide.—G. Lion.

MEETINGS FOR THE WEEK.

Wednesday, Nov. 20.—Society of Arts, 8. First Ordinary Meeting. Opening Address of the 136th Session by the Duke of Abercorn, C.B., Chairman of the Council, and Presentation of Prizes.

AMERICAN MINERALS.

After the close of the Universal Exposition

Prof. A. E. FOOTE

will remain at his Branch,

14, RUE DESAIX, PARIS,

until the 15th of December. Here he will be glad to meet collectors and to fill all orders received previous to that time. He finds it necessary to prolong his stay in Paris for the purpose of giving attention to the numerous orders for Minerals which have been received by mail, and which he could not fill on account of being constantly occupied with customers at his branch.

Many of the rare and choice Minerals shown at his Exhibit during the Exposition will be removed to his store. Here also will be found the most beautiful Red Vanadinites ever seen, with Crystals remarkable for large size and brilliant colour, and at very low prices; really showy specimens are sold at from 2s. to 5s. Also beautiful Red Wulfenites from Arizona; fine single crystals are sold at from 1s. to 5s. Among the other remarkable Minerals are Gadolinite, Colemanite, Hanksite, Thenardite, Apophyllite, Sperryllite, Beryllionite (new Glucium Species described by Dana), &c.

Specimens sent on approval. Especial attention is called to these beautiful minerals for Christmas and other presents.

Prof. FOOTE has, at his principal store, 1223, BELMONT AVENUE, PHILADELPHIA, U.S.A., the largest stock of Minerals, Chemical, and other Scientific Books for sale in the world, and will exchange for good minerals or for books. Send for Catalogue, specifying in what branch you are interested.

THE CHEMICAL NEWS.

Vol. LX. No. 1565.

AN EXPERIMENT IN COLOUR-BLINDNESS.*

By JOHN SPILLER, F.I.C., F.C.S.

Examination of several colour-blind persons having convinced me of the practical value of a compound tassel of green and grey silk cords as a preliminary indicator of defective colour-vision; and, moreover, having studied Professor William Pole's interesting memoir—describing his own case—in the *Philosophical Transactions of the Royal Society*, April, 1859, which is illustrated by a diagram, showing bands of "neutral grey" appearing to him in the middle of the green and at the deepest red, or crimson, of Chevreul's coloured *cercle chromatique;* I felt very desirous of trying an experiment to see for myself whether it was possible by the administration of a small dose of santonine—which is said to cause temporary colour-blindness—to realise in my own case the imperfection of vision which seems common to most colour-blind patients.

Such an experiment I made on the 29th of August; but before proceeding to describe the result it should be mentioned that I have good proof of my being blessed with the possession of a normal sight; for in the course of a long experience with coal-tar colours, and having frequent occasion to compare observations with regard to slight differences of tint with my six colleagues, I have never perceptibly deviated from the consensus of the laboratory staff, and may fairly claim to be reliable on this score. On a fine day, provided with an ample selection of chemical specimens and coloured objects, and Ladd's direct vision spectroscope ready to hand, I took, fasting, a small dose of santonine, a grain and a half, dissolved in a small quantity of alcohol and diluted with water. In less than five minutes the drug had taken effect; the white table-cloth appeared of a delicate bluish green colour—pale turquoise, exactly like the colours of the *Nineteenth Century Magazine*, and all objects were seen as through spectacles of that precise tint. A rapid survey was made of my varied collection of objects, and I went into the garden to use my spectroscope. I could see all the solar colours in unbroken series with scarcely perceptible variation; the Fraunhöfer lines were there as usual (not thickened), the violet extending up to the usual limit, and so with the red end, with slightly diminished brilliancy, but hardly appreciable absorption; there was *no neutral grey band in the green*, but this portion of the spectrum appeared quite normal and splendidly brilliant. The observation was repeated a few minutes later with the same results.

Turning to my coloured specimens. Nickel, copper, and iron sulphates, iodide and chromate of lead, ultramarine, and ammonio-sulphate of copper, were quite normal; oxalate of cobalt had not lost its delicate pink colour, nor nitrate of uranium its well-known shade. On the other hand, scarlet iodide of mercury was decidedly dulled, and a fine sample of carmine appeared more like crimson. By running my eyes along the book shelves in my library, I soon noticed that "Gmelin's Chemistry"—Cavendish Society series—and other old-fashioned green bindings assumed a kind of slatey appearance, crimson backs appeared as maroon, dark brown was converted to chocolate, but I could see violet quite well, bright green pretty much as usual, the Chemical News, bound in scarlet, appeared red, and neutral grey bindings looked only darker in colour. I could see quite distinctly the difference between light-green and slate-grey silk tassels, so that my condition was not so abnormal as many of my colour-blind friends, who fail to see any radical tint-distinction between these two dissimilar colours.

Now for a word of caution. I had taken only what might be described as a quarter-dose—"2 to 6 grains" is the stated quantity in "Martindale's Extra Pharmacopœia"; other authorities say more—but at the end of fifteen or twenty minutes, the tension upon my nervous system proved so serious that I feared the worst consequences. I felt so giddy and depressed, with a kind of mild tetanus, that I was obliged to resort to an emetic—mustard and warm water,—which soon gave me relief. I would earnestly warn my readers of the danger of repeating this experiment; and now, on fuller enquiry, I learn that santonine is a drug reported to be "sometimes uncertain in its action," and occasionally developing "poisonous symptoms from its depressing effects on the nervous system." I had read of Dr. W. G. Smith taking a 5-grain dose to induce colour blindness—"Cooley's Cyclopædia of Practical Receipts," p. 1460—without dangerous consequences, and resolved to take a very much smaller quantity, 1½ grain, in the first instance, well knowing that more than this had often been given to children. Perhaps taking it in the state of solution, and before breakfast, or a wrong dose, made all the difference. However that may be, I shall never again try ophthalmic experiments with santonine, and would warn others against doing so without proper medical advice.

My object is accomplished: I wanted to search for Professor Pole's neutral grey bands in the solar spectrum, as he sees them in Chevreul's famous *cercle chromatique* diagram, but did not find them. Nor, it may be added, do any of my colour-blind friends see any break in the solar spectrum, although we know that the heavy green pigments are by them so often mistaken for grey. Furthermore, it does not appear that santonine gives the *same kind* of colour-blindness as commonly presented by the natural defect, or my colour test of green and grey would at once have indicated it.

London, September 2, 1889.

* Read before the British Association, Section A Newcastle Meeting.

INTERNATIONAL STANDARDS FOR THE ANALYSIS OF IRON AND STEEL.

The Committee, which was appointed at the Bath meeting with the object above mentioned, requested the co-operation of several gentlemen of special experience in the analysis of iron and steel, and is at present constituted as follows:—Professor Roberts-Austen (Chairman), Sir F. Abel, Professor Langley, Mr. Edward Riley, Mr. G. J. Snelus, Mr. John Spiller, Professor Tilden, and Mr. Thomas Turner (Secretary).

The Committee has held several meetings during the year, and considerable correspondence has taken place in connection with the matters which it was appointed to consider. Ultimately, the objects of the committee were defined, and a number of suggestions were drawn up in order to assist in carrying out these objects. These suggestions were then published in various technical papers, before being finally revised, in order to allow persons interested to make any further suggestions which might appear advisable, After revision these proposals assumed the following form:—

Objects.

It is proposed that the Committee shall co-operate with other similar Committees in the more important iron-producing countries, in order to provide standard

* Report of the Committee, consisting of Professor Roberts-Austen (Chairman), Mr. T. Turner (Secretary), and Professor J. W. Langley, appointed to consider the best method of establishing International Standards for the Analysis of Iron and Steel. Drawn up by Mr. Thomas Turner (Secretary). Read before the British Association, Section B, Newcastle Meeting.

specimens of iron and steel, the chemical composition of which shall have been carefully determined. The specimens adopted as standards shall be entrusted to some recognised official authority, such as the Standards Department of the Board of Trade, and shall be used either for reference in the determination of the accuracy of any proposed method of analysis, or for controlling the results of analyses in any cases of importance which may from time to time arise.

Suggestions.

1. Professor J. W. Langley, of the University of Michigan, U.S.A., to be requested to superintend the production of the samples; these to be prepared and preserved in accordance with the directions to be furnished by the Committee, and an equal portion of each sample to be forwarded to the several Secretaries of the respective Committees in the United Kingdom, America, France, Germany, and Sweden.

2. The Specimens, which are eventually to be adopted as standards, to be supplied to not more than seven representative chemists of repute in each of the countries above mentioned, who shall be requested to analyse the specimens by any method or methods they may prefer.

3. In the event of the analyses giving results which, in the opinion of the Committee, may be regarded as sufficiently concordant, the means of the analytical results of each of the several constituents to be adopted as representing the composition of the standards. The report on the analytical results not to be issued before the various analysts to whom the samples have been submitted shall have had an opportunity of examining it. The standards to be hereafter distinguished only by letters or numbers.

4. The attention of the Committee to be for the present confined to five samples of steel, selected as containing as nearly as possible 1·3, 0·8, 0·4, 0·15, and 0·07 per cent of total carbon, respectively. In addition to the determination of the amount of carbon present in each condition, the phosphorus, sulphur, silicon, manganese, and chromium also to be determined.

5. 200 kilos. of the samples selected for examination as standards to be prepared in all. This would give, after allowing sufficient for the required analyses, quite 5 kilos. of each standard for each of the five countries interested. Allowing, say, 10 grms. for each applicant who might desire to use the standards, this would permit of 500 appeals to each of the five standards in each country, or at least 12,500 appeals in all.

6. The metal of which the samples are to be produced to be cast in small ingots, special care being taken to prevent any irregularity of composition. After the removal of the outer skin the metal to be cut by a blunt tool in the form of thin shavings, and mixed as intimately as possible.

7. The samples thus prepared to be preserved in separate small quantities (say of 30 grms. each), which shall be hermetically sealed in glass tubes so as to prevent oxidation.

8. The samples to be analysed, in the United Kingdom, by Mr. A. H. Allen, Sheffield; Mr. W. Jenkins, Dowlais; Mr. G. S. Packer, Steel Company of Scotland; Mr. J. Pattinson, Newcastle-on-Tyne; Mr. E. Riley, London; the Royal School of Mines; and Mr. J. E. Stead, Middlesbrough.

Progress of the Work.

Under date July 14, 1889, Professor Langley states that he has not as yet received a conclusive reply from the State Department at Washington to his application asking the Government to forward the samples through its consular agencies, so that they might reach their destination with the seals of the American Committee unbroken by the Custom House inspectors. The first four standards are ready to go as soon as word is received from Washington. They are packed in lead-lined hermetically sealed boxes, four for each country, and which are enclosed by a larger wooden case, the whole weighing about 400 lbs.

The material was prepared as nearly as possible in accordance with the directions of the British Association Committee. Ingots of crucible steel were selected from a lot of some twenty-five tons, which came nearest to the required carbon for the first three standards. The last, C=0·15, was too low to be made in a crucible, for, after melting up a number of charges, it was not found possible to get below 0·20 in the plumbago crucibles used. Professor Langley accordingly took a large billet of Open Hearth Steel, and, after forging, had a piece weighing about 100 lbs. cut out of the centre.

The original weight of the ingots was 90 lbs., but, after turning off the skin and allowing for the pipe and some inevitable loss in turning, not much over 50 lbs. could be recovered in drillings. This will cause the weight of the standards to be somewhat less than specified, but it seems as though there was no help for it, because to have attempted to make the quantity up from two ingots would have introduced metal of a slightly different carbon, and so brought about an objectionable lack of uniformity.

The metal was turned in a lathe at a very slow speed, and with a blunt tool. The whole time of turning was between three and four months.

In regard to pulverising the drillings as originally proposed, Professor Langley found it utterly impossible to do so by any means which would not introduce a notable quantity of foreign matter. Between chilled rolls the shavings only flattened. They were sifted through a 30-mesh sieve, and the fine material so obtained, which is small in quantity, is in a separate enclosure. The rest of the drillings are as nearly homogeneous as it is possible to make them, because they have been made from "dead melted" stock formed at one heat from a single crucible.

The various Committees are as follows:—Sweden, Professor Richard Akerman, Secretary; Germany, the Government Department of Tests; France, Mons. Ferd. Gautier, Secretary; England, the British Association Committee; United States, three members of the American Society of Civil Engineers, viz., William Metcalf, Thomas Rod, and A. E. Hunt; and three members of the faculty of the University of Michigan, viz., Professors J. W. Langley, A. B. Prescott, and M. E. Cooley.

The material for the standards and the mechanical work on them have been furnished by the Crescent Steel Works of Pittsburgh gratuitously, because of the interest this firm has always shown in promoting the cause of scientific metallurgy.

Professor Langley further says:—"I can make the fifth standard, the 0·08 carbon suggested by your Committee, only it will take probably about two months. I will start upon it in a short time, as soon as I can make the right kind of stock, which will have to be Bessemer, for I can blow a heat as low as that without trouble."

Within the last few days a letter has been received from Professor Langley as representing the University of Michigan, and from Mr. William Metcalf, on behalf of the American Society of Civil Engineers, stating that the samples have been despatched to each of the four countries previously mentioned (Great Britain, France, Germany, and Sweden). It is hoped that the analyses will be commenced almost immediately, and that by the next meeting of the Association the work may be in a forward condition.

Photometry with Nitrogen Iodide.—G. Lion.—The author utilises the decomposition by light of nitrogen iodide prepared by the action of the aqueous solution of pure ammonia at 22° upon iodine. This substance, remaining in the liquid in which it was formed, is slowly decomposed, with an escape of nitrogen proportionate to the intensity of the incident light. He compares the illuminating power of two lights by means of two burettes containing equal quantities of the reagent, and communicating by means of a capillary tube containing a mercurial gauge.—*Comptes Rendus*, Vol. cix., No. 17.

ON WATER ANALYSIS.

By H. M. VERNON.

In Frankland's method of estimating the organic carbon and nitrogen in potable waters by the combustion process, one of the chief difficulties and sources of error seems to occur in the evaporation of the water to dryness. In Frankland's original process of evaporation in a platinum dish on the water-bath, with a covering of filter-paper to keep out the dust and other organic impurity from the air, the evaporation could only be accomplished so slowly that it frequently took two days to evaporate a litre of water to dryness.

We have thus the comparatively unstable nitrogenous organic impurities in the water subjected to a temperature of 100° C. for perhaps fifty hours. It is scarcely possible that some decomposition should not take place under these circumstances. This, indeed, Dr. Frankland admits, and he has even drawn up tables showing the amount of nitrogen lost as ammonia when a water has been evaporated to dryness in the presence of reagents, as phosphorous and sulphurous acids. The amounts given in these tables are to be added to the amount of nitrogen subsequently found by combustion. When the water is evaporated in the presence of sulphurous acid, this amount to be added is about one-fourth of the total quantity of nitrogen found by combustion. When such a large number as this is to be added on to the amount found it is evident that the error in the amount of organic nitrogen really present in the water may be considerable.

These tables mentioned above do not give any information as to the length of time the waters took to evaporate, although this is obviously a very important factor in the determination of the amount of nitrogen to be added on to the amount found by combustion.

It appears that the only way to eliminate these sources of error successfully is to so evaporate the water and obtain the solid residue without the nitrogenous organic constituents in any way undergoing decomposition.

To accomplish this I will mention a very simple method which, I believe, will satisfy these conditions, although I cannot say I have tested it experimentally. It consists simply in evaporating the water under a very small pressure over strong sulphuric acid.

On turning to the tables of the boiling-points of water at various temperatures, it will be seen that water boils at 12° C. under a pressure of 10·457 m.m.; that is, under approximately a pressure of a centimetre. Now, by means of the Sprengel pump it is possible, in a very few minutes, to obtain a pressure far less than this; indeed, with a Sprengel of the ordinary make a pressure of 0·1 m.m. may easily be obtained. If, now, the water to be evaporated be placed in a platinum basin in a desiccator over strong sulphuric acid, and if this desiccator be placed in connection with the Sprengel pump with a vessel of strong sulphuric acid between them to absorb the steam as fast as it is generated, and if the pump be now set in action, so that the pressure in the desiccator is less than 1 c.m., the water in the platinum basin will begin to boil, and will continue to do so until it has evaporated to dryness. By varying the pressure in the desiccator by means of the pump the rate at which the water should boil can be easily adjusted.

In this way, then, it is possible to evaporate the water to dryness without its temperature rising above 12° C., or even less if it be required. It is evident that the nitrogenous organic constituents suffer much less chance of decomposition when the water is evaporated in this way than when it is evaporated at 100° C.; for not only is the temperature of the water never allowed to rise much above 12° C., but also the evaporation takes place in almost total absence of air, and thus again the chances of decomposition of the organic constituents are minimised. A still more cogent argument is, perhaps, the act that by this method the water can be evaporated down in a very few hours, instead of the fifty or so hours required in Dr. Frankland's process. This objection to Frankland's process has, of course, been partly removed by the introduction of Bischoff's method of evaporation.

If the water be evaporated at all fast when the basin is merely placed in the desiccator, such a large amount of heat would become latent, owing to the conversion of water into steam, that in a short time the water would be converted into ice. To obviate this difficulty the evaporation of the water may be carried on in a vessel of glass with double walls. Between these walls a stream of cold water at about the same temperature of the atmosphere is allowed to flow. By this means the temperature of the water in the vessel will never sink low enough for it to freeze, and if the stream of water circulating between the walls be at all rapid it will not sink to more than a degree or so lower than the temperature of the water surrounding it.

It will simplify matters if this double-walled evaporating basin is itself made to answer the purpose of a desiccator, and thus to render unnecessary rhe use of the ordinary form of desiccator. All that is necessary to render this possible is that the evaporating basin should have a broad rim ground smooth; a glass lid, also ground smooth on its under side, is fitted to this, so that an air-tight connection is obtained. In the lid it will be necessary to have a glass stopcock connected with the Sprengel, so that the required pressure may be obtained.

As the quantity of water required to be evaporated would probably be considerable, and it would be inconvenient to have an evaporating basin of the above form large enough to hold it all at once, another hole is made through the lid, and through this projects the end of the tube of a tap funnel. The tube must be fitted into the lid, so that an air-tight connection is obtained. This may be effected either by fitting a caoutchouc cork in the hole and passing the end of the tube through this, or by grinding down both the tube and the hole, so that the one fits accurately into the other. If the stoppered funnel is chosen of such a size that it holds exactly half a litre when filled up to a mark in the neck, it will be easy to evaporate down a half litre or a litre of the water, as the case may be, without any further trouble of measuring.

It will be found more convenient to have the tube of the funnel long and to have two glass taps in it a few inches apart than to have only one tap. The reason of this will be made obvious.

The pressure of the atmosphere is about 760 m.m., while that inside the vessel is only about 10 m.m. If, now, supposing the funnel only had one tap, this tap were opened, this comparatively large pressure upon the water in it would drive the water with considerable force into the evaporating basin, so that probably some of it would be carried over mechanically into the vessel of sulphuric acid used for absorbing the steam from the water, and thus some of the residue would be lost; also, more of the water may enter the basin than it would be convenient to evaporate at a time. If, now, two taps are used instead of one, this difficulty is entirely obviated. Thus, to introduce the water into the evaporating vessel by this means the upper tap is first opened, the lower one being closed; the water runs down the tube and fills the space between the two taps; the upper tap is then closed and the lower one opened; the pressure in the evaporating basin being almost nil, the column of water between the two taps will run down into the evaporating basin and there be evaporated. We have thus introduced a small definite volume of the water into the evaporating vessel without danger of any loss of organic matter, owing to some of the water being carried over mechanically into the vessel containing the sulphuric acid.

In this way, the whole of the water is introduced in small quantities from the funnel into the evaporating vessel, and is there evaporated.

The vessel of sulphuric acid here spoken of is placed between the tube leading from the evaporating vessel and

the Sprengel pump; its purpose is to absorb the steam distilling over from the water as it evaporates. In order that this water may distil over without trouble, the vessel of sulphuric acid should be surrounded by another vessel containing water at a few degrees lower temperature than the water circulating between the walls of the evaporating basin. The quantity of sulphuric acid in the vessel should be considerable, as it has to absorb half a litre or a litre of water.

During the whole of the evaporation the Sprengel must be kept at work; if it were not, the pressure in the evaporating vessel would soon rise, and the water cease to boil; this being due to the escape of the gases dissolved in the water.

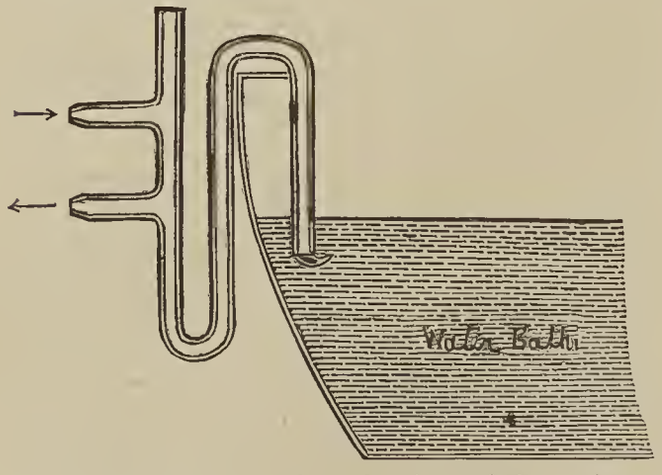
If the residue left after evaporation is required to be weighed, it must be scraped out of the evaporating basin into a weighed platinum basin, and then weighed. A better plan would be employ, during the whole process of evaporation and subsequent weighing, a weighed platinum vessel of the same shape as the interior of the evaporating vessel, and fitting tightly in it. At the end of the evaporation it could be removed from the evaporating basin and weighed.

It must be remembered that this method of evaporation is, so far, entirely theoretical, as I have not myself at present the means for testing it experimentally; it is brought forward merely as a suggestion, and it is hoped that it will be received as such.

A SIMPLE WATER-BATH REGULATOR.

By T. H. EASTERFIELD, B.A., F.C.S.

THE apparatus represented by the accompanying figure is a simple and effective arrangement for keeping the water in water-baths at constant level. The idea is possibly old, but seems unknown in the laboratories with which I am acquainted.

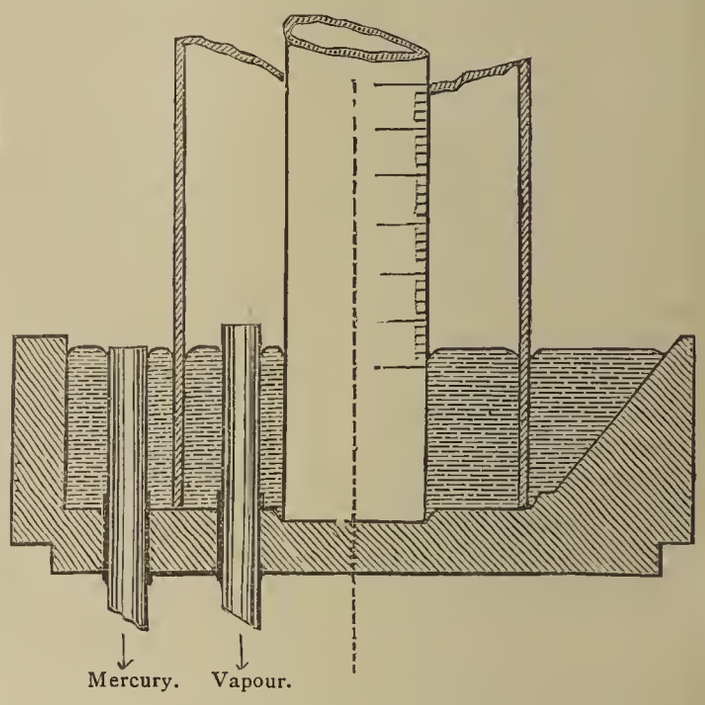


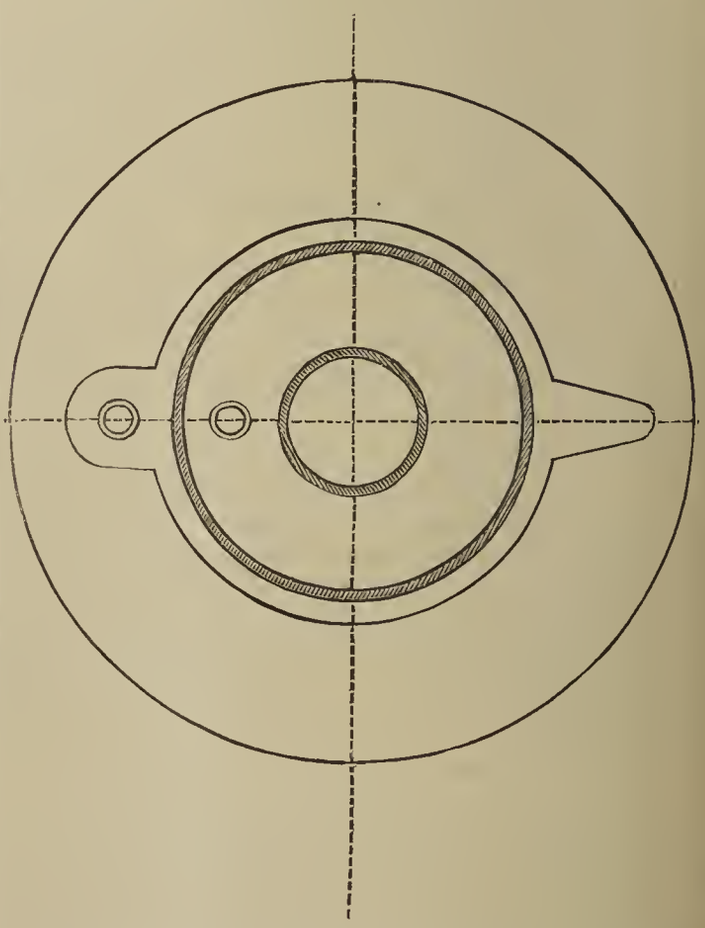
The arrangement consists of a piece of glass tube, open at each end, bent twice, parallel to itself, and having two side-tubes sealed into the longest limb. The upper side-tube admits the water supply, the lower is the overflow-pipe. When the tube has once been filled with water, by turning on the water supply and stopping the overflow-pipe for a moment, the instrument acts as a continuous syphon, keeping the water-level constant.

A HANDY TROUGH FOR HOFMANN'S VAPOUR-DENSITY APPARATUS.

By T. H. EASTERFIELD, B.A., F.C.S.

THE accompanying figure represents a cheap and effective trough for use in determining vapour density by Hofmann's method. It consists of a thick disc of wood turned to fit tightly into the ring of an ordinary retort stand, and hollowed out in the manner shown in the section. Through the bottom of the trough pass two glass tubes, kept in place by bits of rubber tubing. One of these glass tubes lies outside the steam-jacket, and serves for the escape of the mercury, which runs away, clean and dry, into a bottle placed to receive it. The second tube passes into the steam-jacket and leads away the steam and condensed water.





The trough is, of course, made to just fit any particular size of steam-jacket, and should be just large enough to allow the operator to work conveniently. The arrangement ensures that the lower level of the mercury shall be approximately constant; very little mercury is required, and that which runs away is perfectly clean.

The apparatus has been tried for two years in the

Cambridge University Chemical Laboratory, and also in the Würzburg Physical Laboratory, and has given great satisfaction.

NEW OBSERVATIONS ON THE RECIPROCAL DISPLACEMENTS BETWEEN OXYGEN AND THE HALOGENS.

By M. BERTHELOT.

The author has indicated how the reciprocal displacements between oxygen, on the one hand, and, on the other hand, the halogens, chlorine, bromine, iodine, combined either with metals or non-metals, or with hydrogen, are foreseen by the thermo-chemical theory, and verified exactly by experiment, and he has lately extended these relations to fluorine. He now purposes explaining the interpretation of various reactions of the same order, more delicate, and effected at the ordinary temperature, commencing with hydrochloric acid.

The formation of dilute hydrochloric acid from its elements (H+Cl) liberates +39·3 cals., whilst that of liquid water (H + O) liberates only 34·5 cals. Hence oxygen does not decompose dilute hydrochloric acid in the cold, whilst chlorine decomposes water at the ordinary temperature, with the simultaneous formation of the oxy-acids of chlorine, as theory indicates. But hydrochloric acid gas possesses, on the contrary, a formation-heat of +22 cals., lower than that of gaseous water (+29·5 cals.), at least at ordinary temperatures, for at 2000 the two quantities become equal, and at still higher temperatures the formation-heat of hydrochloric acid gas predominates. Hence various reactions and equilibria, which have been studied elsewhere ("Essai de Mécanique Chimique, ii., p. 500). Theory indicates that these equilibria may be manifested at ordinary temperatures on operating suitably, for instance, with fuming hydrochloric acid, which is a mixture of various hydrates with the anhydrous acid. Still it has not been found that this acid, when perfectly pure, undergoes any decomposition in the cold, even if exposed to a moderate solar light.

It has been found that the reaction in the cold may be determined by adding to the hydrochloric acid certain metallic chlorides, the influence of which, assimilable to what was known of old as actions of contact, results in reality in the formation of intermediate compounds, which serve as steps towards the completion of the reaction. Such, in particular, is manganous chloride. After placing, in a large flask full of air, about 20 c.c. of very pure fuming hydrochloric acid, the flask has been exposed for several weeks to the sun without either the air or the liquid acquiring the odour of chlorine, or the power of decolourising a dilute solution of indigo. But if there are added to the liquid a few decigrms. of pure manganous chloride, it gradually becomes coloured, even in diffused light, or better in the sunlight, and it acquires the brown tint of the compound which precedes the formation of chlorine in its preparation by the action of hydrochloric acid and manganese peroxide, or, it might be said, the hydrochlorate of manganese peroxide which has been described in the *Annales de Chimie et Physique*, Ser. 5, vol. xxii., p. 464. This tint augments for several days, up to a certain limit. At the same time the air above is charged with gaseous chlorine and the liquid below acquires bleaching properties.

This formation of chlorine results from the absorption of ordinary oxygen by the liquid, and from the dissociation of manganese perchloride hydrochlorate, formed in consequence of this absorption, and of the presence of an excess of hydracid not saturated with water. If the chlorine in the air above is eliminated and replaced by hydrochloric acid mixed with oxygen, the phenomenon is reproduced, and it is clear that it may be reproduced indefinitely by reason of a known mechanism of dissociation, which incessantly regenerates a new dose of free chlorine, of hydrochloric acid, and of manganous chloride. But if we do not introduce hydrochloric acid the reaction will stop about the point where there only exist hydrochloric hydrates saturated with water, such that the gas no longer possesses any appreciable tension. In fact, the author has found that hydrochloric acid diluted with water, and not fuming, is no longer decomposed by oxygen, even in presence of manganous chloride.

Manganous chloride is especially apt to produce these phenomena. With ferric chloride added to fuming hydrochloric acid we obtain signs of reaction, but almost insensible and difficult to show.

Reactions of the same order intervening equally, with formation of dissociated intermediate compounds, occasion the displacement of the chlorine in hydrochloric acid by the oxygen of the air, and latterly it has been industrially utilised on the large scale.

We see, by these observations, how energies in some sort latent, and capable, in principle, of producing exothermic phenomena, but which, in fact, do not produce them under given conditions, may be rendered manifest by the intervention of certain agents acting only as intermediate stages, and capable of developing indefinite reactions. Here is the whole thermo-chemical theory of action of presence.—*Comptes Rendus*, cix., No. 15, p. 546.

ON COMMERCIAL QUERBRACHO EXTRACT AND ITS DETECTION.

By J. A. WILSON.

It occurred some time since to the writer that the presence of certain alkaloids in querbracho might prove of advantage in detecting the extract from that wood in dyewood extracts, such as logwood, berry, fustic, &c. On page 99 of Allen ("Commercial Organic Analysis," vol. iii.), *Aspidospernum Querbracho* is mentioned as the source of the commercial extract, but I am informed that Querbracho Colorado is the one most generally used.

Commercial querbracho extract is said to be mixed with other astringent drugs, and palmed off as extract of querbracho, so that if the presence of the alkaloids were proved in the genuine extract, the amount in these doctored extracts would be very variable. However, I determined to see whether any alkaloids could be obtained from the commercial extract, as manufactured by first class firms, and two samples were therefore examined in the same manner as used for detection of glucosides and alkaloids in general. Sample No. 1 gave me:—

1·86 per cent ash (0·81 soluble, 1·03 insoluble). Alkalinity of soluble equal 0·37 per cent K_2O.

30·47 per cent total non-volatile solids.

The total solids on extraction gave—

3·2 per cent petroleum ether extract.
50·7 ,, alcoholic extract.

Fifty grms. of the extract was examined for alkaloids in the following manner:—

1. Evaporation in a vacuum at 50° C.

2. Residue treated with 150 c.c. of 90 per cent alcohol acidulated for eighteen hours.

3. Treating the residue obtained on evaporation of alcohol with six times the volume of water for twelve hours and filtering.

4. Treating the filtered liquid from 3 with immiscible solvent, petroleum ether, benzol, chloroform, &c., in the acid state.

5. The liquid, after extraction in the acid state, is rendered strongly alkaline with ammonia, and extracted as before with petroleum ether, benzol, and chloroform; the latter quite warm.

The residues obtained on evaporation and recovery of solvent were then examined by the general group reagents, and by the sulphuric acid and lead peroxide test, also by sublimation.

I may say that I failed to detect the least trace of any alkaloid whatever.

The Laboratory,
Tottington, near Bury.

PURIFICATION OF HYDROFLUORIC ACID FOR USE IN ANALYSIS OF SILICATES, &c.

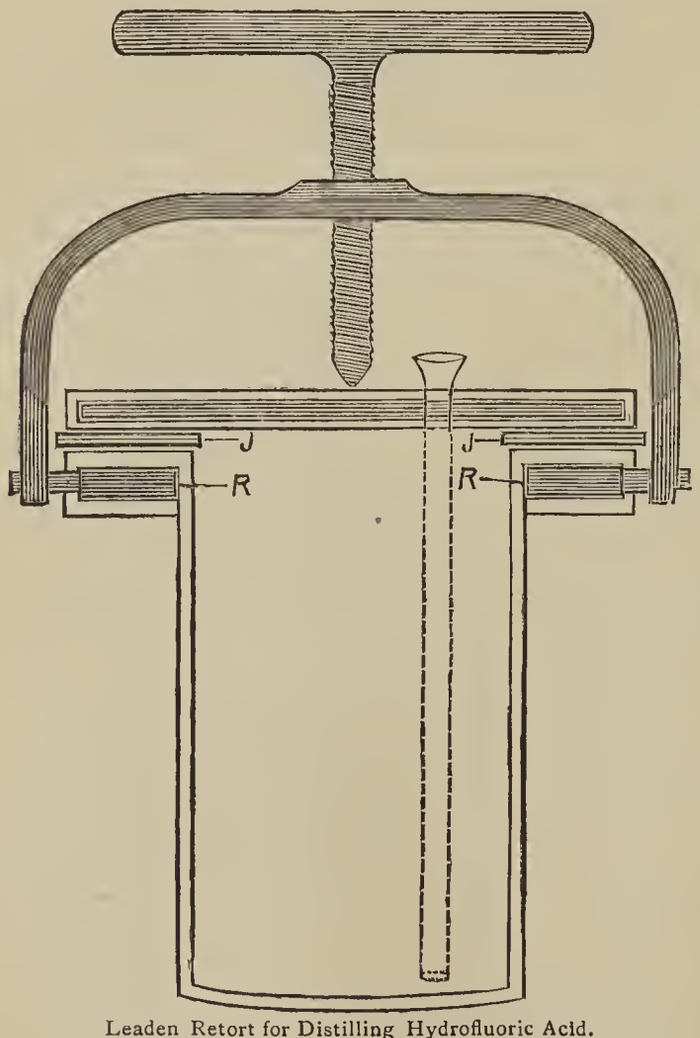
By ROBERT HAMILTON, F.I.C.

HAVING for two years used the process for the analysis of silicates almost as described by George Craig (CHEMICAL NEWS, lx., 227), I can testify to its usefulness, speed, and even elegance ; its accuracy has been long established.

FIG. 1.

Arrangement of Nose of Retort for Distilling Hydrofluoric Acid.

FIG. 2.



Leaden Retort for Distilling Hydrofluoric Acid.
R, Wrought iron ring, 1 in. × § in.; J, India-rubber ring joint.

The leaden retort adapted by me to the distillation of the commercial hydrofluoric acid fulfils its purpose extremely well, and I submit a sketch of it in the hope of facilitating the adoption of the process.

The body of the retort is 6 inches high by 4 in diameter, of heavy sheet-lead, and a broad seat is formed for the sheet india-rubber joint, J, by beating the lead back over an iron ring, R, 1 inch wide by §-inch thick. Two projections, from opposite sides of the ring serve to secure the ends of the iron bridge (1 inch wide by §-inch thick), which is the main feature of the retort. The lid is made of ¼ inch iron plate covered with lighter sheet lead. All the lead joints are burned.

The remainder of the sketch is self-explanatory. It will be observed that the leaden nose of the retort points upwards, and that the india-rubber tube is carried a little higher, to ensure that no dissolved lead is carried down.

For condenser, I use thin-walled black india-rubber tubing, of $\frac{3}{16}$-inch bore, connected to the leaden nose by stouter tubing of larger bore, and passing through india-rubber corks in ends of Liebig's condenser case. The crude strong acid rapidly attacks and destroys the india-rubber tubing, and should be diluted till it contains about 25 per cent HF, when an acid comes over of very convenient strength for analytical work.

After charging the retort, I heat it in the stink-box, attach a short piece of india-rubber tubing to the nose, and at frequent intervals place the free end of the tube in water, till silica (of which there is usually a little) ceases to separate. The retort is then transferred to the condenser, and, after a little regulation of the heat, the distillation proceeds quietly and smoothly, and becomes one of the easist of laboratory operations.

Flocks of sulphur, which sometimes separate, may be removed by letting the distillate filter through paper, in a vulcanite funnel, into the india-rubber receiver.

Eglinton Iron Works,
Ayrshire, N.B.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING OCTOBER 31ST, 1889.

By WILLIAM CROOKES, F.R.S.;

WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford ;

and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, November 9th, 1889.

SIR,—We submit herewith the results of our analyses of the 189 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from October 1st to October 31st inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

Of the 189 samples examined, the whole were found to be clear, bright, and well filtered.

Throughout the past month of October the supply of water to the Metropolis has continued to be of excellent and very uniform character, the proportion of organic carbon in any single sample of Thames-derived water

examined varying only from 0·135 to 0·155 part in 100,000 parts of the water; with a mean of 0·143 part, as against a mean of 0·138 part in the previous month's supply,—the absolute difference of 0·005 part in 100,000 parts of the water being wholly insignificant.

In respect also to its clearness, its degree of freedom from colour-tint, and its minute proportion of matter oxidisable by permanganate, the October water supply has well sustained the satisfactory character presented by the supply of the previous month.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 7th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. John Burgess, 7, Wellington Road, Peckham; William Frederick Britcher, 33, Tranquil Vale, Blackheath; Frank Hill Perry Coste, Ravenshoe, Burnt Ash Hill, S.E.; David Brown Dott, 104, South Canongate, Edinburgh; Robert Stephen Edwards, B.A., Gwern-y-Gaseg, Minera, Wrexham; James Kerr Erskine, 6, Lascotts Road, Wood Green, N.; John Foggie, Newport, Fifeshire, N.B.; Harold Gripper, 77, Cecil Street, Greenhays, Manchester; H. B. Helbing, German Hospital, Dalston; Robert Edward Hughes, 15, Clare Street, Canton, Cardiff; James Robert Kaye, 33, Great Charles Street, Birmingham; Henry Richard Kerwood, M.B., Frogmore Broadelyst, Devonshire; Frederick Thomas Knott, The Laurels, Eltham Road, Lee, Kent; L. Napier Levingham, Brightside Steel Works, Sheffield; G. B. Mason, Barbados, West Indies; James Braik Mason, 3, Park Terrace, Dundee; Thomas Mercer, Great Hey, Edersfield, near Bury, Lancashire; Joseph Alfred Nettleton, East Grinstead, Sussex; Wallace Christopher Nickels, 14, Yew Grove, Cricklewood, N.W.; James Gordon Parker, Penketh, near Warrington; Alfred Edridge Pike, Westminster Medical School, S.W.; William Ping, 2, Sandbourne Road, Brockley, S.E.; Frederick Quincke, Ph.D., 13, Portland Terrace, Regent's Park, N.W.; Sydney Augustus Sworn, 3, Peel Street, Bedford; Willis G. Tucker, M.D., Albany, N.J., U.S.A.; Daniel Walker, School of Mines, Ballarat, Victoria; Matthew Whittam, St. Peter's School, York; Basil P. Wigan, Macclesfield; John Wilkie, 20, Buckingham Street, Charing Cross; John Wiltshire, Knowsley Cottage, Torre Park, Torquay.

The following papers were read:—

87. "*Isolation of a Tetrahydrate of Sulphuric Acid Existing in Solution.*" By S. U. Pickering.

The freezing-points of mixtures of sulphuric acid and water form three distinct curves, representing the crystallisation of water, of $H_2SO_4 \cdot H_2O$ and of sulphuric acid respectively; in each of them the highest point is in exact correspondence with the composition of the substance which crystallises out. No solutions containing between 75 and 40 per cent of acid had yet been frozen, but it appeared to the author that if his former deductions from the irregularities in the curves representing the densities and other properties of solutions of the acid were correct, an independent curve representing the crystallisation of a new hydrate should occupy this interval, and that this new hydrate could only be either $H_2SO_4 5H_2O$ or $H_2SO_4 4H_2O$. Experiment has proved that it is the latter. The two branches of the new curve obtained rise from about −80°, and meet in a sharply marked angle at a point exactly corresponding to the composition of the tetrahydrate, the temperature at which this point is reached being −25°. The tetrahydrate forms large, well-defined, hard crystals.

Apart from the consideration that the isolation of this hydrate was the direct outcome of his having previously recognised its existence in the dissolved state, the author maintains that the crystallisation of a substance from a liquid necessitates the recognition of its existence in that liquid. The various possibilities are (1) that the solid constituents solidify separately in the proper proportions, and subsequently combine: this view is obviously untenable; (2) that the molecular aggregates constituting the solid are formed directly from the acid and water: this means that a hydrate has no fundamental molecule, and, besides, leaves the impossibility of explaining how these solid aggregates can hunt each other out, and congregate to form large crystals; (3) that fundamental molecules of the hydrate are formed in solution, but cannot remain there, and consequently separate out almost immediately: this is tantamount to saying that the hydrate is an insoluble substance, a proposition which could scarcely be maintained even if the substance were not crystalline; (4) that the molecules of the hydrate are formed in the liquid, and exist there till the temperature is lowered below its freezing-point. This, in the author's opinion, is the only tenable hypothesis.

When a liquid freezes and melts at a definite temperature, when the temperature remains constant till the whole of the liquid is frozen, when any alteration in its composition lowers its freezing-point, we have the most certain evidence yet adduced for regarding that liquid to be a definite, though, possibly, somewhat dissociated, compound. If we deny this argument as applied to the hydrate in question, we must deny it in all cases, and conclude that no liquid is a definite substance.

The author does not argue that the mere fact of the existence of the liquid hydrate at −25° implies its existence at the higher temperatures (8—38°) at which his density and other determinations were made; on the contrary, he argued that because it existed at the higher temperatures it must exist at the lower ones, and having proved this to be a fact he holds that the premisses from which his conclusions were drawn must be correct.

The author believes that the dihydrate may yet be obtained as a solid, since there is a reach of 7 per cent in its vicinity where freezing-points have not yet been attained. He has also isolated another hydrate which crystallises in small quantities with the monohydrate, but has not succeeded in determining its composition.

88. "*Additional Observations on the Magnetic Rotation of Nitric Acid and of Hydrogen and Ammonium Chlorides, Bromides, and Iodides in Solution.*" By W. H. Perkin, Ph.D., F.R.S.

In his previous experiments (*cf.*, *Proc. Chem. Soc.*, 1889, p. 83), the author had limited his observations on nitric acid to the pure acid, HNO_3; he has now examined a somewhat diluted acid, and the results obtained indicate that HNO_3 unites with water, forming an acid analogous to orthophosphoric acid, viz., $(HO)_3NO$.

The experiments on hydrogen chloride, bromide, and iodide were originally made on single samples in a very concentrated solution of each. These gave abnormally high results—rather more than twice the values calculated for the pure compounds—but on examining solutions of different strength it was found that the rotation *increases* up to a dilution equivalent to about 6 or 7 mols. of water to 1 mol. of hydride, the value then remaining practically stationary. To see whether the solvent had any influence, a solution of hydrogen chloride in isoamyl oxide was examined, and was found to give values nearly identical with those calculated from the chlorine derivatives of the paraffins; and there can be little doubt that if

the other hydrides could be examined in a similar way analogous results would be obtained. As union with water should reduce the rotations, the results at present are quite inexplicable.

The compounds with ammonia and the compound ammonias have been also further examined; the results are remarkable when considered in relation to those afforded by the hydrides, as the rotations found, instead of being those calculated from the results obtained in the case of paraffin-derivatives, or those *found* in the case of hydrogen chloride dissolved in isoamyl oxide, nearly correspond to those required on the assumption that the hydrides are present in aqueous solution together with ammonia. The rotations, however, do not vary with the strength of the saline solutions. The author's explanation of this is that when the salts are dissolved in water they dissociate almost entirely into the hydride and the amine, the hydride undergoing an increased rotation on account of its being in aqueous solution. In the case of triethylamine chlorhydride the numbers are lower, and there is evidently less dissociation; and in the case of tetrethylammonium chloride little or no dissociation appears to take place. Solutions of ammonium iodide and diethylamine chlorhydride in absolute alcohol gave somewhat lower numbers than aqueous solutions, indicating a somewhat smaller although large amount of dissociation.

As already noticed, ammonium nitrate gives numbers very close to the calculated; apparently it does not dissociate to any appreciable extent. As the author was not satisfied with the numbers obtained for neutral ammonium sulphate, the acid sulphate was examined, and this gave the calculated numbers; these, when compared with those for the neutral salt, show that the latter undergoes dissociation to a small extent when in solution, which is in agreement with the well-known fact that its solution in water gives off ammonia when heated. The examination of these oxy-salts shows clearly that the salts containing hydrogen chloride, bromide, and iodide, when in aqueous solution, are in a very abnormal condition, but a condition which is easily explained if they are in a state of dissociation.

Discussion.

Dr. Gladstone said that when the refraction equivalents of the hydrides of the halogen elements and of nitric and sulphuric acids in solution were first determined, it was observed that the values were far higher than those calculated; but on re-examining hydrogen chloride solutions he had recently found that as the amount of water was increased a slight increase in the specific refraction also set in quite analogous to that described by Dr. Perkin. The whole subject of the behaviour of such substances in solution deserved a full and deliberate investigation with reference especially to the possible occurrence of dissociation. He had little doubt that some dissociation did occur in the case of the ammonium salts. As it is well known that increase of temperature greatly promotes dissociation, it would be well to repeat the observations at various temperatures in order to learn whether a change takes place in the refraction and magnetic rotation. On examining Dr. Perkin's solution of hydrogen chloride in amyl oxide, he found that the refraction and dispersion values deduced for the chloride are very much smaller than those afforded by aqueous solutions: thus another case of correspondence between the three properties of magnetic rotation, refraction, and dispersion of light was made evident.

Professor Ramsay, referring to the high values observed by Dr. Perkin in the case of dilute solutions, drew attention to recent speculations concerning the occurrence of atomic dissociation in solutions, and asked, might not the high values be explained by assuming that hydrogen chloride underwent dissociation into hydrogen and chlorine atoms?

Dr. Armstrong said that although it might be argued from the results obtained with aqueous solutions, that atomic dissociation attended dilution, the fact that normal values were obtained when amyl oxide was used as solvent was evidence of the insufficiency of such an explanation, and clearly indicated that the water played an active part; according to the now fashionable dissociation hypothesis, the solvent acted merely as a diluent, as one gas does to another, dilution corresponding to reduction of pressure; on this hypothesis, therefore, the values obtained should be the same for solutions of equivalent strength in either solvent. Dr. Perkin's results appeared to indicate that a certain proportion of the water molecules —those which were carried round, as it were, by the hydrogen chloride molecules — underwent what might be termed *extra* rotation. Dr. Perkin based his conclusion that hydrates would afford lower and not higher values on the results which he had obtained in the case of compounds such as the hydrates of nitric and sulphuric acids, and of aldehyd, and of chloral; but these were all hydrates of compounds containing polyad elements; the behaviour of monad elements might well be peculiar. In fact, in discussing these questions, valency must be taken carefully into consideration. Dr. Gladstone had suggested that observations should be made at various temperatures; such observations would undoubtedly be of importance, and might even be expected to afford a final settlement in favour of one or the other hypothesis. If the increased rotation be conditioned by hydrates, as such hydrates would undergo dissociation on heating, the values would diminish as temperature rose; but if atomic dissociation took place, the change would be in the contrary direction, although, as the effect of temperature in promoting atomic dissociation is often not very marked until a somewhat higher temperature is attained, the effect of moderate heating would not necessarily be exhibited by an increase of the rotation.

89. "*Phosphoral Trifluoride.*" By T. E. Thorpe, F.R.S., and F. J. Hambly.

The authors find that phosphorus oxyfluoride, POF_3, may be easily and conveniently made by heating a mixture of cryolite ane phosphoric oxide, and collecting the products at the mercurial trough. The interaction appears to be strictly analogous to that by which Kolbe and Lautemann obtained phosphorus oxychloride by heating phosphoric anhydride with common salt;—

$$2P_2O_5 + 3NaCl = POCl_3 + 3NaPO_3$$

(*Ann. Chem. Pharm.*, cxiii., 240).

90. "*Acetylation of Cellulose.*" By C. F. Cross and E. J. Bevan.

By heating cotton cellulose with acetic anhydride and zinc chloride (Franchimont, *Ber.*, xii., 2059) the authors have obtained a product which, judging from the results of analysis and the proportion of acetic acid which it yields when submitted to alkaline hydrolysis, appears to be a *pentacetyl* derivative of cellulose; the yield was found to be 83 per cent of that calculated for a pentacetate, and the insoluble product of hydrolysis exhibited the behaviour of a normal cellulose. The compound is very stable, being re-precipitated unchanged from its solution in a mixture of nitric and sulphuric acids. It would appear, therefore, that all the oxygen of the cellulose molecule acts as hydroxylic oxygen. In discussing the bearing of these results, it is pointed out that the evidence upon which substitution of OH in the cellulose molecule has been assumed to be at a maximum with the triacetate (Schutzenberger) and trinitrate, is insufficient. Franchimont's representation of the molecule of cellulose as an aggregate of "glucose" groups, condensed according to the equation $n(C_6H_{12}O_6) - (n-1)H_2O$ (R.T.C., ii., 241), is based upon strong evidence, but affords no suggestion of the mode in which the condensation takes place. The extreme inertness of cellulose, as evidenced by the fact that it does not interact with acetic anhydride at its boiling-point, but only at a temperature of 180°; its resistance to the powerfully hydrolytic action of acid sul-

phites at high temperatures; together with the results detailed in this communication, go to show that it is probable that cellulose represents a type of carbon compound *sui generis*.

Discussion.

Dr. Armstrong remarked that present ideas as to the constitution of cellulose are mainly an extension of our views concerning carbo-hydrates of the cane-sugar and dextrin groups: we are accustomed to regard these latter as etheric-derivatives of the glucoses and to look on cellulose as a compound of a somewhat similar type; but its physical properties, its behaviour on acetylation, and the peculiar condition under which alone it undergoes hydrolysis, serve to indicate that perhaps it is a compound of a different and special type, as the authors of the paper suggest may be the case. In seeking to formulate the constitution of cellulose, the possibility that it may even be a closed chain compound should not be entirely overlooked, the occurrence of compounds such as inosite and quinic acid—both derivatives of hexhydrobenzene—in plants being not without significance from this point of view.

91. "*Action of Light on Moist Oxygen.*" By Arthur Richardson.

The author finds that the presence of liquid water very much facilitates the oxidation of many substances under the combined influence of sunlight and oxygen. If, however, the water is present as aqueous vapour, the decomposition is exceedingly slow, and in some cases is entirely arrested.

He finds that peroxide of hydrogen is formed when water containing pure ether is exposed to light in an atmosphere of oxygen; on shaking some of the ether with a solution of potassium bichromate, the ether at once assumed a decided blue colour.

From an extended series of experiments the following facts have been observed:—(1). The amount of hydrogen dioxide formed depends on the proportion of ether to water present. (2). No dioxide is formed when a mixture of water-vapour, ether-vapour, and oxygen is exposed to sunlight. (3). No dioxide is formed when water and ether are exposed in an atmosphere of carbon dioxide. (4). No iodine is liberated from potassium iodide by a mixture of water, ether, and oxygen from which light has been excluded.

On exposing pure water, acidified with pure sulphuric acid, to light, hydrogen dioxide was found in the solution; this was estimated by permanganate of potassium. Water exposed to rays of low refrangibility gave no hydrogen dioxide.

On placing water which contained the dioxide, immediately after exposure to light, in the dark, it was found, after some time, to be free from dioxide; but hydrogen dioxide was formed on again exposing the solution to light; this process could be repeated indefinitely.

From these and other experiments the author is led to believe that the oxidation of substances under the influence of light involves in many cases initially an oxidation of water to hydrogen dioxide, and that the oxidation of the compound is the result of a secondary interaction between it and the hydrogen dioxide.

Discussion.

Dr. Armstrong said that it had long since been stated that peroxide of hydrogen was formed when ether and water was exposed to atmospheric oxidation; Mr. Kingzett had brought the subject under the notice of the Society several years ago (*cf. Chem. Soc. Journ.*, Abstr., 1877, p. 183). Dr. Richardson assumed that the water was directly oxidised; Mr. Kingzett had argued—and in the case of turpentine had adduced weighty experimental evidence—that the hydrogen peroxide was a secondary product, formed by the action of water on an organic peroxide. It was impossible to say from Dr. Richardson's results which explanation was the correct one; perhaps neither was wholly correct, as it was not impossible that the conjoint influence of the water and ether was an essential feature of the interchange with oxygen. Dr. Richardson had added ether or sulphuric acid with the object of protecting the peroxide from decomposition; surely weak solutions of hydrogen peroxide were not so unstable that proof could not be obtained of its formation if it really were produced on exposing water and oxygen to light. There was no satisfactory evidence that it was formed in the absence of a third substance. In the case of the experiments made without ether, it was just possible that the minute amount of organic matter present in the water—perhaps that derived from stoppers—had been effective in promoting peroxidation; the disappearance of the peroxide in the dark tended to favour this view.

Professor Thorpe said that he had recently had occasion to satisfy himself that water played an important part in promoting peroxidation. It had long been known that the atmospheric so-called ozone reactions were at least principally due to hydrogen peroxide; finding in the Admiralty instructions the statement that the air of the Hebrides was said to contain more ozone than any air in the world, he had, during a recent yachting tour there, exposed Schönbein paper at various distances above sea level; he had always found that, after six hours' exposure the "ozone" manifestations were very much stronger five or six feet above the sea than some distance above the sea, at the mast-head of the yacht.

Professor Ramsay drew attention to the fact that when a substance capable of destroying hydrogen dioxide was present, the peroxide might be formed and immediately thereafter destroyed. Such was probably the case in polluted rivers; and it might well be that the continual formation and decomposition of hydrogen peroxide was the effective cause of the oxidation of organic matters in waters. Its formation apparently tended towards a maximum, which, in presence of matter capable of decomposing it, would never be reached (*cf.*, *Proc. Chem. Soc.*, 1886, p. 225).

Mr. Groves remarked that weak solutions of hydrogen peroxide were by no means unstable, but would keep for months.

Professor Dunstan asked whether Dr. Richardson had proved that the oxidising substance was hydrogen peroxide. He had made a series of experiments which showed that it was not formed when *pure* ether was used, although a substance was produced which was capable of liberating iodine.

Dr. Thorne, referring to the possible effect of a third substance in influencing oxidation, said that he had had occasion to observe that in bleaching coloured fibres a solution of 75 per cent strength of hypochlorite in presence of oxygen gave the same results as one of 100 per cent strength used alone.

The question was asked whether the precaution had been taken in the experiments with potassium iodide to exclude carbon dioxide from the air.

The President said that in experiments which he and Captain Abney had made together on the fading of water-colours, the action of aqueous vapour had been most strikingly apparent; colours were found to be stable on exposure to light in dry air, which were considerably affected when aqueous vapour was present.

Dr. Richardson, replying, said that the bichromate test indicated that the substance formed in presence of ether was hydrogen peroxide. Using pure water, he had obtained traces of peroxide, which, however, could not be estimated. In some cases the bottles in which the exposure to light was effected were provided with glass stoppers. He thought that very little was known as to what happens when iodine separates from potassium iodide: the solution does not exhibit an alkaline reaction.

(To be continued).

NOTICES OF BOOKS.

Chemical and Physical Studies on the Metamorphism of Rocks. Based on a Thesis with Appendices written for the Doctorate in Science in the University of London. By A. Irving, D.Sc., B.A., F.G.S. London: Longmans, Green, and Co.

Geology has of late years undergone a transformation approximating to that which has been witnessed in biology, and of a similar nature. In the hands of Dr. Irving and of like-minded investigators it is being elaborated on that grand principle of evolution which is re-animating all the sciences.

We hope it will not be considered an unpardonable digression if we notice the very advanced views regarding higher education which the author puts forward in his preface. He writes:—"The departure which our University (London) has now made in recognising original work and in doing its part in lifting the discussion of higher scientific questions out of the professional arena . . . . augurs well for the future of science in this country. It may be questioned whether the outcry referred to (that against cram and examinationism?) is not, to a great extent, a reflex of a belief in that system of over-teaching which has done so much to check the growth of original scientific thought in this country, as compared with some of the leading nations of the civilised world, by giving too much advantage in the academical race to mere receptivity." Most true; but is it not a radical error to make the academical career a "race"? The author proceeds:—"It seems to be forgotten at times that the truest 'teaching' is that which stimulates the mind to active thought, not that which saves the student the trouble of thinking by loading the memory with second-hand knowledge. One necessary consequence of this is seen in the rareness of appeals in a great deal of the scientific literature of this country directly to nature as compared with the quotation of names of authority as giving weight to certain views." He continues, more questionably:—"There are reasons for doubting whether, with the exception of the Royal Society, there is a single scientific society in London which is entirely free from the interested influence of a close profession." We think such societies can be found, because some such bodies are not built on lines coinciding with the limits or the interests of any profession.

But we must unhesitatingly agree with Dr. Irving when he says:—"Those on the other hand to whom it has been given to experience the regenerating influence of Nature upon the human intellect will acquit me of any suspicion of cant when I say that above and beyond any honours which it is in the power of any academical body to bestow, nay even beyond and above the appreciation of one's work by one's own contemporaries, research confers its own reward in the healthy habit of mind which it induces."

Turning to the body of the work we find, after some preliminary explanations, in which the author complains very justifiably of the vagueness of existing nomenclature, a discussion of paramorphism, or mineral change, of metatrophy, or changes in the physical characters of rock-mass, and of metataxis, or changes of order of the constituents of the rock-mass. He criticises such utterances as that of Mr. Green, that, according to his (the author's) theory "the constituents of those rocks (the archean crystalline schists) were supposed to have been held in solution in an ocean of boiling water, and to have been deposited as it cooled." He considers that any geological argument which "proceeds on chemical and physical lines" is, in some quarters, unduly depreciated.

In treating of the metataxic work done by solar and lunar tides, the author objects to one of the results put forward by Prof. R. S. Ball. That eminent astronomer concludes that some millions of years years ago the tidal wave must have been several hundred feet high. This might be granted if we assume that the quantity of water condensed on the globe was the same as it is now. But the author tells us that this, on Prof. Ball's own showing, we have no right to do. He quotes Zoellner's view of five successive stages in the life of worlds: (1) the nebulous phase (condition of glowing gas); (2) the glowing liquid phase, as in fixed stars with constant brilliancy; (3) development of a solid glowing crust, as in fixed stars of variable brilliancy; (4) bursting of the thin crust and extensive eruption of the glowing fluid interior; (5) the gradual thickening of the solid crust and condensation of water upon it.

On our globe this last stage must be the Cambrian era. In connection with this subject we note a remark which will be welcome to judicious workers in every branch of science:—"It must be recollected that the output of the mathematical mill will depend upon what is put into it." If we put in visions the result will be dreams.

In his conclusions the author insists that it is a vain and useless task to think of finding any one principle of metamorphism. He thinks it evident that the earth must have, in the course of its development, passed through a *pre-oceanic* stage. He regards the archean series of rocks as representing, upon the whole, the primordial earth's crust, from which the siliceous materials of the sedimentary rocks have been for the most part derived, and considers that "one more chapter is thus added to the history of that great Law of Evolution which is written upon all created things."

In a note Dr. Irving calls attention to the relations, at once of contrast and of similarity, existing between silicon and carbon. Will they ever, as Brown hoped, be found mutually convertible?

Chemists, we think, will feel a deep interest in the study of the work before us from the able and successful manner in which the author applies chemical laws to the elucidation of geological problems.

Watts' Dictionary of Chemistry. Revised and entirely Re-written by M. M. Pattison Muir, M.A., and H. Forster Morley, D.Sc., assisted by Eminent Contributors. In Four Volumes. Vol. II. London and New York: Longmans, Green, and Co.

We are glad to find that the publication of the new edition of Watts's great work is making good progress. The present volume extends from chenocholic acid to indigo, inclusive, and comprises such important subjects as classification, dissociation, earths, elements, chemical equilibrium, equivalency, formulæ, geological chemistry, and indigo.

As a general rule, the information supplied is on a level with the most recent discoveries, in as far as these can be regarded as definitely established. In some cases, indeed, the views taken by the different writers are not absolutely in accordance. Thus, the author of "Earths" speaks decidedly of neodymium and praseodymium as "elements." In the article "Elements," on the other hand, we find these two bodies referred for the present to a provisional class, such as "meta-elements."

If a choice can be made among the longer articles, all of which are of high ability, the article on "Elements" must bear the palm. The author evidently inclines to the belief that the simple bodies of chemistry have been formed from something still simpler, or possibly from one primary form of matter, by some process of evolution not yet understood. The arguments in favour of this new view are summarised clearly and forcibly, but impartially. The writer is of opinion, however, that if "a transmutation of so-called elementary matter should ever be effected in the laboratory, it will be by the very slow development, under conditions of prolonged chemical stress, of change in traces only." In other words, if transmutation is effected, it will not be in some sudden manner, capable of being exhibited on the lecture table, and still less will it admit of industrial execution.

In discussing Prout's law, he concludes that some law approximating to, if not identical with, that proposed by Prout, actually exists.

Under "Cobalt," we find no discussion of its alleged decomposition into two bodies, the true cobalt, and an accompanying impurity, which, as Dr. Krüss alleges, is also found accompanying what has hitherto been regarded as pure nickel.

Germanium and its compounds are very fully and carefully treated; and the same must be said of gallium.

Decipium is regarded as doubtful, and Davyum is mentioned as requiring re-investigation. Didymium is also a subject for doubt: if an element, it is referred to Group V., along with N, P, and eepecially Bi. Concerning its supposed components, neodymium and praseodymium, it is remarked that if salts of the two are mixed in certain proportions the spectrum is the same as that of didymium. This is not quite the case, as the spectrum of didymium contains a residual band not to be found in either that of neodymium or praseodymium.

Two features of the book deserve especial notice, as likely to prove a great convenience to the reader. One is that to several of the more important articles there is appended a carefully compiled bibliography of the subject; the other is a flexible card attached to the binding by ribbon, and capable of serving as a book mark; upon it are printed the many abbreviations, both of the names of journals and transactions cited as authorities, and of the technical terms employed. By these abridgments a great economy of space is effected, and the idea of placing them so as to obviate the frequent references to the beginning of the volume seems to us exceedingly happy, and will be generally appreciated, as will be the work altogether.

CORRESPONDENCE.

THE "AMINES" SEWAGE PROCESS.

To the Editor of the Chemical News.

Sir,—"Cyclops" is in error again. In his last letter (Chem News, lx., p. 245), he suggests, after conceding all my claims as to the *effects* of "Aminol," that by these very effects the "Amines" sludge is rendered useless as a *manure*, because the combined nitrogen which it contains can become available as a plant food only by decomposition or *nitrification*.

The facts are these:—*Putrescrible* sludges, unless *speedily* reduced to dryness (which involves expenditure) waste their nitrogen in the process of putrefractive decomposition. The "Amines" sludge, on the contrary, being *non-putrescible*, preserves all of its nitrogen and may be dried slowly and inexpensively by simply spreading it on land. When sufficiently air dried, its nitrogen becomes available for *nitrification* in the soil, when applied as manure. So much for the value of the sludge as to nitrogen. How about the other plant foods constituting the value of a manure, such as potash, phosphoric acid, and last, but not least,—lime? Is "Cyclops" not aware that lime "is a *direct* plant food; that no crop can grow to perfection without lime, that it favours the formation of nitrate of potash in the soil; that the functions of lime in living plants are connected with the building up of the tissues and the formation of the cell walls, and that its mechanical effect upon coarse sandy, as well as upon fine alluvial soil, and also upon peaty and upon clay lands, is highly benificial and of vast importance?" (See Griffith, on Manures, pp. 232—248).

"Cyclops" is also wrong in assuming that the formation of Aminol *alone* governs the quantity of lime used in the "Amines" process; the degree of clarification required and other considerations play an important part in the determination of the proportions.

"Cyclops" gives it as his opinion that from 45 to 50 grains of lime per gallon are quite impracticable quantities when applied to large flows of sewage; he does not, however, support this opinion by argument. My experiments, per contra, have established not only the entire practicability, but even the true economy of the proportions which I employ.

Allow me to suggest, in conclusion, that your correspondent's criticisms might be better appreciated were he to sign his real name, like—Your Obedient Servant,

Hugo Wollheim.

The "Amines" Syndicate, Limited,
101, Leadenhall Street, London, E.C.
November 18, 1889.

MILK ANALYSIS.

To the Editor of the Chemical News.

Sir,—In reply to Mr. Alf. W. Stokes, can he prove my statements to be wrong? The original Wanklyn method I know, the Somerset House method I know, and the Soxhlet plaster-of-paris method I know; but I have had little or no experience in the Soxhlet areometric process, and much less of the lactocrite.* I therefore regret extremely I cannot comply with Mr. Stokes's request and give him the information he desires. The Schmid process has been under my consideration for some considerable time, but I must confess I have been unable to obtain such concordant results as those obtained by Mr. Stokes. However, I may mention, for Mr. Stokes's benefit, that I have a modification of Schmid's method, giving very satisfactory results, and which I hope to make use of at some future date. Mr. Stokes states:—"It is singular that all these should agree with the calculated results." Why should they not? One would naturally expect them to do so when the particular formula is employed which belongs to that particular process.

I said nothing about "the now generally discarded Wanklyn method," which has long been known not to give accurate results.

Might I now ask Mr. Stokes to give us a series of comparative results obtained from the various processes he has mentioned in his communications to you, and also the formulæ he uses to obtain the calculated results.—I am, &c.,

William Johnstone.

City Central Laboratory,
13, Fish Street Hill, Nov. 17, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 18, October 28, 1889.

The Equilibrium of Distribution of Hydrogen between Chlorine and Oxygen.—H. Le Chatelier.—The author gives a formula of equilibrium for a mixture of oxygen, chlorine, water, and hydrochloric acid.

Certain Double Nitrites of Ruthenium and Potassium.—A. Joly and M. Vézes.—The author has obtained two double nitrites, which do not agree in composition with those of an analogous compound obtained by Claus.

Fixation of Nitrogen by Leguminous Plants.—E. Bréal.—Nodosities may be produced on the roots of such plants by pricking them with a needle which has previously been plunged into a nodosity of another plant o

* By Harold Faber the lactocrite is inaccurate when used on skim-milk to the extent of 0·2 per cent.

the same family. The nodosities are full of bacteria, which enable the plant to fix atmospheric nitrogen. An experiment was made with haricots sown in gravel and sand free from nitrogen. The plants were watered with a known quantity of water, containing less than 0·100 grm. of nitrogen. The nitrogen fixed by the plants was 1·4872 grms., and that absorbed by the soil 0·4810, or a total of 1·9682 grms. The cultivation of leguminous plants during the last two years enables the author to conclude, in accordance with Hellriegel, Wilfarth, and Berthelot, that these plants can grow and develop themselves in soils poor in nitrogen if their roots are furnished with nodosities, by means of which they are able to fix atmospheric nitrogen. Hence they are justly called ameliorating crops.

On Ground-Air.—Th. Schlœsing, Jun.—All other things being equal, the proportion of carbonic acid varies considerably at different points. On slopes near the bottom of a valley the air is richer in carbonic acid at the lower points than at the upper. The ground-air must not be supposed to be in a state of rest.

On Sorbite.—C. Vincent and M. Delachanal.—All the fruits of the *Rosaceæ* contain sorbite, along with a sugar capable of fermentation. From pears the authors have obtained 8 grms. of sorbite per kilo., and from cherries grms.

Researches on Crystalline Digitaline.—M. Arnaud.—Crystalline digitaline is a definite chemical species, and there is no reason for designating the pure product as digitoxine. It seems to be the type of a series of analogous bodies, among which must rank tanghinine.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iii., September. 1889.

Experimental Researches on the Periodic Law.—H. Bohuslav Brauner.—From the *Journal of the Chemical Society*.

Properties of Selenic Anhydride.—Messrs. Cameron and Macallan.—Taken from the CHEMICAL NEWS.

Falsifications of the Vegetable Oils of Commerce.—Paul S. Girard.—A continuation of a valuable memoir, which does not admit of abstraction.

Nitrate of Soda and the Nitrate Country.—Ralph Abercromby.—From *Nature*.

Assay of Palm and Copra Oils.—Calixte Ferrier.—The fatty acids derived from the decomposition of these oils saturate a much larger proportion of base than do the fatty acids from the oils of olive, colza, earth-nut, sesame, linseed, poppy, &c. The fatty acids of palm oil and copra may be split up by crystallisation from alcohol, by pressure, and by fractionated distillation. The following quantities of normal potassa are required for saturating the various fatty acids:—Palm, 21·8 c.c.; copra, 23·6; cotton, 18·4; earth-nut, 17·8; olive, 18·0; sesame, 17·7; tallow, 17·6; lard, 17·4; resin (Bordeaux), 13·2.

Nut Oil.—Th. Bruce Warren,—From the CHEMICAL NEWS.

Gymnemic Acid.—D. Hooper.—From the CHEMICAL NEWS.

Determination of Free Alkali in Soaps.—A. Wilson.—From the CHEMICAL NEWS.

New Theory of the Double Elliptical Refraction of Quartz.—Dr. G. Quesneville.—A mathematical paper, having no direct bearing upon chemistry.

Recognition of Blood.—W. P. Mason.—From the CHEMICAL NEWS.

The Great Chemical Industry at the Exhibition of 1889.—P. Kienlen.—An account of the manufactures of sulphur from different sources, of carbon disulphide, and of sulphurous acid, the sulphites, and the hyposulphites.

On Thiocamf—A New Disinfecting Agent.—Emerson Reynolds.—From the CHEMICAL NEWS.

Industrial Society of Mulhouse.—Session of the Chemical Committee, July 10, 1889.—A new salt of antimony, bearing the name of vomitartarine, and made by Finck, of Stuttgart, was exhibited and handed over for examination to M. Schœelhammer.

R. Bourcart gave a communication on the use of uranium acetate as a mordant for silk and wool.

A sample of tempered mica was submitted to the meeting, and will be examined by M. Camille Schœn.

M. Fehr finds that the diazosulphonic acids obtained by the double decomposition of diazo-chlorides with sodium bisulphite remain unchanged in presence of alkaline phenols as long as the mixtures are kept in the dark, but combine with the formation of oxy-azo- colouring-matters under the influence of the solar rays. Trials made with a certain number of chemical agents (both oxidisers and reducers) to effect combination gave no result.

The Presence of Tin in Certain Sugars, the Means of its Detection, and its Possible Influence upon Public Health.—Dr. Phipson.—From an English source, which is not named.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Lump Camphor.—Can any correspondent tell me of a manufacturer in England of "lump" camphor?—MEDICUS.

MEETINGS FOR THE WEEK.

MONDAY, Nov. 25th.—Medical, 8.30.
—— Society of Arts, 8. (Cantor Lectures). "Modern Developments of Bread-making," by William Jago.
TUESDAY, 26th.—Royal Medical and Chirurgical, 8.30.
—— Institute of Civil Engineers, 8.
WEDNESDAY, 27th.—Society of Arts, 8. "Scientific and Technical Instruction in Elementary Schools," by J. Hall Gladstone, Ph.D., F.R.S.
THURSDAY, 28th.—Institute of Electrical Engineers, 8.
SATURDAY, 30th.—Royal, 4. (Anniversary).

Water-Glass, or Soluble Silicates of Soda and Potash, in large or small quantities, and either solid or in solution, at ROBERT RUMNEY'S, Ardwick Chemical Works, Manchester

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FOR SALE.—THE CHEMICAL GAZETTE. Complete Set (unbound and uncut), 17 volumes; from November, 1842, to December, 1859.—Address, "Publisher," CHEMICAL NEWS Office, Boy Court, Ludgate Hill London, E.C

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THE CHEMICAL NEWS.

VOL. LX. No. 1566.

A NEW PROCESS FOR THE VOLUMETRIC ESTIMATION OF BROMINE IN PRESENCE OF CHLORINE AND IODINE.

By NORMAN McCULLOCH.

IT may not be that the new process to be described will be considered as possessing superior practical features to the best yet devised for the accurate estimation of bromine in presence of chlorine; but if only as projecting a little novelty on the solution of this problem, no apology need preface its publication.

It takes its origin in a new method for volumetrically estimating iodine in presence of chlorine and bromine (CHEM. NEWS, vol. lvii., p. 135), a process which consists in the titration of the hydrochloric acid solution of the iodine or iodide with standard permanganate until the free iodine is converted to the colourless monochloride, a point indicated by means of chloroform.

This procedure is also applicable, although with only approximate accuracy, to the estimation of bromine. The solution to be examined is placed in a glass stoppered bottle, mixed with about one-third of its bulk of strong hydrochloric acid, and a little chloroform added as indicator. The whole is now titrated with permanganate, shaking well after each addition, until the colour of the chloroform ceases to grow paler. The sources of error in the method are due, firstly, to want of sharpness in the end reaction; secondly, the reducing influence of the chloroform on the free bromine and chloride of bromine; and thirdly, formation of a small proportion of manganic chloride, a compound which does not instantaneously react with bromine to the formation of manganous chloride and chloride of bromine.

I use the above method for approximating the amount of bromine to be determined by the more accurate process now to be described, and the facts underlying which are briefly as follows:—

I. When permanganate is added to hydrochloric acid containing a sufficient proportion of manganous chloride, manganic chloride (Mn_2Cl_6) is formed—no chlorine being liberated—*and this compound is unacted upon by hydrocyanic acid.*

II. Bromine and iodine, free or combined with hydrogen, reduce manganic chloride, and are converted to the monochlorides; thus, in the case of hydrobromic acid:—

$$HBr + Mn_2Cl_6 = HCl + BrCl + 2MnCl_2.$$

III. Chlorine, bromine, iodine, and their compounds with each other are reduced by hydrocyanic acid, and as shown in the followlng typical equation:—

$$2Cl + HCN = HCl + CnCl.$$

Taking the facts so far, it follows that when permanganate is added in excess to a hydrobromic and hydriodic acid solution containing the required proportion of manganese chloride, hydrochloric acid, and hydrocyanic acid, chloride, bromide, and iodide of cyanogen are ultimate products of the reaction.

The formation of these compounds may be considered as preceded by that of manganic chloride,—

$$8MnCl_2 + 16HCl + K_2Mn_2O_8 = 5Mn_2Cl_6 + 2KCl + 8H_2O$$

(a reaction in which, I think, oxidation of the manganese precedes its conversion to manganic chloride), this compound then reacting with the bromide and iodide, to the consequent formation of the monochlorides of bromine and iodine, and reduction of these by the hydrocyanic acid—

$$HBr + HI + 4HCN + 2Mn_2Cl_6 = CrBr + CrI + 2CrCl + 4MnCl_2.$$

It will now be understood that, as the amount of manganic chloride reduced is in proportion to that of the bromine or iodine present, the estimation of the non-reduced salt will enable us to calculate the amount of these halogens. This estimation can readily be effected, and by means of the iodine process alluded to in the opening of this article. Excess standard potassium iodide is added to the solution, then a little chloroform, and the whole titrated with standard permanganate until the violet colour of the indicator is discharged. The reaction may be equated thus:—

$$Mn_4Cl_6 + 2HI = 2MnCl_2 + 2I + 2HCl.$$

$$10I + 16KCl + K_2Mn_2O_8 = 10ICl + 2KCl + 2MnCl_2 + 8H_2O.$$

I may also point out that a little of the iodide of cyanogen will take part in the reaction; so—

$$CNI + HI = HCN + 2I,$$

but without, in the nature of the process, having any effect on the ultimate result; and I have shown, in my experiments on the method (and further proved by recent unpublished results), its applicability to the estimation of iodine in presence of hydrocyanic acid.

Hydriodic acid has no action on chloride and bromide of cyanogen, at any rate under the conditions of my process.

I trust that the principle of my method for volumetrically estimating bromine is now clear, and I may proceed to the details of its application.

The required standard solutions of permanganate and potassium iodide are of decinormal and seminormal strength respectively.

The former is prepared by dissolving 31·9 grains potassium permanganate in 10,000 grms. of water; and, as the salt is never quite pure, the solution requires standardisation, which is most accurately and conveniently effected as follows:—

A known weight of from 3 to 5 grains pure dry iodine is dissolved in a little caustic soda Aq contained in glass-stoppered bottle of about 5 ozs. capacity, acidulated with ½ oz. or so of strong hydrochloric acid, the stopper replaced, and bottle and contents cooled. The permanganate is now run in until the solution is nearly decolourised, a little chloroform added, and the violet colour communicated to this by the free iodine liberated, discharged by further but more cautious titration with the permanganate, shaking well after each addition.

The discharge of iodine colour from the chloroform indicates—what already has been equated—conversion of the free iodine to the colourless monochloride by the chlorine liberated in the reaction of the permanganate with the hydrochloric acid.

The iodine equivalent of the permanganate is calculated to bromine by multiplying by the factor 0·6713, and each division (10 grains) equals about 0·04 grain Br considered as the hydracid.

The potassium iodide solution (82·78 grains KI in 10,000 grains H_2O) is also standardised, and with the permanganate by the foregoing process for iodine. Bulk for bulk, it should be equivalent to the permanganate, and likewise delivered from a burette graduated to tenths of a division.

The other reagents requiring note are chloroform, a three per cent solution of hydrocyanic acid, and a strong solution of manganous chloride.

The chloroform—pure or methylated—is treated to dispose of any oxidising or reducing constituent by being well shaken with a few divisions of the permanganate and sufficient hydrochloric acid to decompose this. Enough potassium iodide to liberate free iodine is now added, and the colour so communicated to the chloroform discharged by just the requisite amount of permanganate. Finally, the chloroform is washed free, or nearly free, from acid liquor.

The hydrocyanic acid is simply a potassium cyanide

solution decomposed with excess hydrochloric acid, and titrated with permanganate until it acquires a faintly permanent pink colour, in order to destroy oxidisable impurity. Six hundred grains of KCN (95 per cent) are dissolved in 13½ ozs. of water, transferred to solution bottle, and cooled to as low a temperature as conveniently possible, to which end a frigorific solution consisting of ammonium chloride and potassium nitrate in equal bulks, dissolving in water, may be employed. Two and a half ozs. of hydrochloric acid are diluted with their own volume of water, cooled as foregoing, and added to the cyanide solution—an operation which should be performed in a draught, or well ventilated acid chamber. At this point, any carbonates present in the original cyanide will conduce to loss of HCN, through evolving carbon dioxide; and since these experiments it has occurred to me that it would be advantageous to treat the cyanide solution before acidulation with excess barium chloride and filter off the precipitated carbonate.

The acidified solution is cooled, if warm, to the ordinary temperature of the air, and titrated with permanganate until permanently pink in colour.

The manganous chloride solution consists of a half-pound of the crystallised salt ($MnCl_2+4H_2O$) dissolved in 4 ozs. of warm water and cooled; it contains, per vol., 58 per cent of manganous chloride ($MnCl_2$). The use of a manganous salt for the purpose herein described recalls that in connection with Marguerite's process for estimating iron, to prevent the inimical action of free hydrochloric acid; in both cases the prevention of the liberation of free chlorine is the object desired, and to this effect the manganous salt must bear such a proportion to the free hydrochloric acid as to react with the permanganate before the latter has time to bring about its own ultimate effect in the liberation of free chlorine. A solution containing one-third of its volume of strong hydrochloric acid is amply provided with the salt ($MnCl_2$) in the ratio of three molecules to four of the hydrochloric acid (HCl), and will do with less on lowering its percentage of acid by dilution. From 300 to 500 grains of the manganese solution have been used in my estimations, and an ounce will suffice even in the case of the greatest convenient amount of bromine likely to be determined—3 grains or so; it is impossible to err in the way of using too much, barring the inconvenience of a bulky solution, but too little would mean high results.

We do not find, however, that manganese chloride prevents the liberation of free chlorine in the well-known spontaneous decomposition of manganic chloride. Presumably the unstable chlorine atoms in the contiguous molecules of manganic chloride combine to form free chlorine, and free chlorine is unable to effect direct combination with chloride of manganese; the consequence of this is that manganic chloride is not absolutely stable even at low temperatures. Its rate of decomposition is accelerated by heat and the presence of hydrocyanic acid; but, under the conditions of my process, is sufficiently slow for all practical requirements. For instance, the manganic chloride from the reaction of about 30 divs. permanganate does not undergo appreciable decomposition within half an hour, but in double that time may do so to the extent of about one-tenth of a div., and proportionately more for a longer time.

I used as the standard bromide in my estimations pure sodium bromide, prepared by distilling excess bromine, in presence of potassium bromide, into a pure caustic soda solution, evaporating to dryness, calcining at a low red heat, and preserving in a well stoppered bottle.

The estimations were conducted in a bottle same as described in connection with the standardisation of the permanganate.

The weighed bromide was dissolved in a quantity of water, not exceeding half an ounce in volume, and treated with about an ounce of the manganese solution. The standard permanganate was run in, and in excess of from 10 to 30 divs. of the theoretical requirement. The bottle was then plunged into a frigorific solution—such as already described (and of which a handful of the salts dissolving in a few ounces of water sufficed)—for several minutes to cool its contents to a temperature not exceeding 55° F. Thereafter the bottle was removed and a rotary movement imparted to its contents, and hydrochloric acid slowly added to dissolve the manganic hydroxide; usually about half an ounce of strong HClAq was added, the point being to ensure a sufficiency, or about one third, certainly not less than one-fourth in bulk of the total volume of the solution. Excess of the hydrocyanic acid—30/60 grains—was then added, the bottle re-corked and replaced in cooling solution, and time allowed for the reaction to complete, for which half an hour sufficed when the excess of permanganate was as stated, and ensured from an approximate determination of the bromine by the quick and convenient method already described. The solution was then titrated with standard iodide until it became nearly quite decolourised from the complete decomposition of the manganic chloride, and then slightly re-coloured from liberation of free iodine, indicating excess of the iodide by about half a div. Lastly, the excess iodide was accurately determined by adding a little chloroform and titrating with permanganate in the usual way.

The bromine is calculated simply by taking the difference between the amounts of bromine represented by total permanganate and iodide used.

The results tabulated are the latest obtained. Each div. of the permanganate solution was equivalent to 0·0392 grain Br, considered as the hydracid (HBr), as likewise that of the standard iodide.

Br taken. Grms.	I taken. Grms.	Standard $K_2Mn_2O_8$ used.	Standard KI used.	Br found. Grms.
1·024		35·2	8·8	1·034
0·784		31·2	11·2	0·784
1·032		40·6	14·3	1·031
0·287		11·8	4·6	0·282
1·941		80·4	30·8	1·945
0·287		15·9	8·8	0·278
2·717		80·2	10·9	2·716
0·132		15·4	11·7	0·145
0·271		13·3	8·2	0·278
0·442	0·634	30·2	8·8	0·439
0·450	1·891	50·4	8·9	0·435

It will be seen from the two experiments footing the list in the above Table, that iodine, when present, was, of course, determined as bromine, and so had to be allowed for; consequently where the bromine is in association with iodine the latter must be separately determined by the permanganate-hydrochloric acid method, in order that this deduction be made.

The volumetric process is applicable to the estimation of bromine in presence of all substances with which, so far as my knowledge goes, it is likely to be commercially associated, excepting, of course, oxidising and reducing agents and metals forming bromides insoluble in dilute hydrochloric acid.

To the above results, testifying its accuracy, I couple the assurance of its, comparatively speaking, great convenience.

Laboratory of Clyde Iron Works,
(by Tollcross) Glasgow.

Royal Institution.—The Christmas Lectures (adapted to a Juvenile Auditory) will this year be given by Professor A. W. Rücker, F.R.S., Professor of Physics in the Normal School of Science and Royal School of Mines, on "Electricity." They commence on Saturday, December 28th.

NOTE ON THE

COLORIMETRIC METHODS FOR THE DETERMINATION OF NITRATES IN POTABLE WATERS.

By Dr. SAMUEL RIDEAL,
Lecturer on Chemistry at St. George's Hospital.

Having recently had occasion to estimate the amount of nitrates present in some exceptionally pure waters, we have had an opportunity of comparing the results obtained by the well-known colorimetric estimation, based on the formation of ammonium picrate and commonly called the "phenol sulphuric acid" method, with that recently described by S. C. Hooker, in which the intensity of the green colour, produced by the addition of a solution of carbazol to the nitrate solution, is a measure of the amount of nitric acid present. Although the former of these has been known for some years, and our method of performing the operations is not very different from that originally proposed by the author, the following details may be of interest to the readers of the Chemical News:—

The solutions required are (*a*) standard potassium nitrate solution containing 0·7215 grm. of the pure crystallised salt in a litre of water or 1 c.c. = 0·0001 grm. nitrogen; (*b*) phenol sulphuric acid solution prepared by dissolving 15 grms. of pure crystallised phenol in 92·5 c.c. of pure re-distilled sulphuric acid free from nitrates diluted with 7·5 c.c. of water.

In addition to the above solutions, pure strong re-distilled sulphuric acid and dilute ammonia solution are also required.

The process adopted was as follows:—A known volume of the water (100 c.c. or 25 c.c., according to its supposed richness in nitrates) is evaporated to dryness in a porcelain dish. To the dry residue 1 c.c. of the phenol sulphuric acid is added, and then 1 c.c. of pure water and 3 drops of strong sulphuric acid, and the mixture gently warmed. A distinct yellow colour then appears if the water contains any appreciable quantity of nitrates. The contents of the dish are then diluted to about 25 c.c. and ammonia added in slight excess. The solution is poured into a narrow Nessler tube (14″ × 1″), the dish washed, and the washings added to the liquid in the tube, and the whole diluted to the 100 c.c. mark. The colour of the solution is roughly judged, and is then imitated by repeating the operation with the standard potassium nitrate solution, the quantity of which may vary from 6 c.c. for bad waters to 0·1 c.c. for a water fairly free from nitrates.

Under the above conditions the method yields very good results, but care must be taken, if the preliminary evaporation is not conducted over a water-bath, not to heat the solid residue obtained, and also after adding the reagent and acid the mixture must only be very gently warmed.

The phenol sulphuric acid solution should be prepared some little time before use, as the fresh solution imparts a faint greenish tinge to the yellow of the ammonium picrate, which may mislead the eye accustomed to the ordinary tints obtained by this process. It was found impossible to estimate the colour by means of solutions of ammonium picrate; but Lovibond's tintometer was not tried.

In the carbazol method the standard potassium nitrate solution and pure sulphuric acid are also required as well as the following special reagents:—

(*a*). Silver sulphate solution containing 4·3945 grms. per litre or one in which 1 c.c. will precipitate 1 part of chlorine per 100,000 from 100 c.c. of water.

(*b*). Aluminium sulphate solution free from chlorides and iron, 5 grms. per litre.

(*c*). Carbazol Solution.—0·6 grm. carbazol is dissolved in glacial acetic acid, and the solution made up to 100 c.c. with the glacial acid. For use, 1 c.c. of this solution is withdrawn by a pipette and mixed with 15 c.c. of pure re-distilled sulphuric acid.

It was also found advisable to prepare, as the author recommends, a series of solutions containing 0·03, 0·05, 0·07, &c., parts of nitrogen per 100,000 from the standard nitrate solution by diluting with water. The process is as follows:—To 100 c.c. of the water, the amount of chlorides in which has first been ascertained, sufficient of the silver sulphate solution is added from a burette to precipitate all the chlorides. To this solution, containing the silver chloride in suspension, 2 c.c. of the aluminium sulphate solution is added, and the whole made up to a convenient bulk, 110 c.c. in the case of waters containing 1 to 6 parts of chlorine per 100,000. The solution is then filtered, and 2 c.c. of this filtrate are then taken for the nitrate estimation, and, of course, the amount found must be calculated from the diluted bulk of the solution. To the 2 c.c. of the filtered water contained in a test-tube, 4 c.c. concentrated sulphuric acid is added, and the mixture well cooled. 1 c.c. of the carbazol solution in sulphuric acid as above described is then added, and a bright green colour appears in a few moments if nitrates are present. The amount of nitrate is roughly gauged from the colour produced, and 2 c.c. of the standard nitrate solution, considered to be equal to it, is placed in a second test-tube, and the operation repeated with it and a fresh 2 c.c. of the water under examination at the same time. If the tints are not similar a fresh comparison must be made, and in every case it is necessary to repeat the operation with a fresh quantity of the water, so that the colours may be developed as nearly as possible simultaneously.

The author states that 0·0006 m.grm. of nitrogen as nitrate may be detected by the carbazol method. The removal of chlorides is necessary for accurate results, but the filtration does not take much time when aluminium sulphate solution is added as described. As the waters under examination were free from iron, we had no opportunity of noticing the effect of the presence of iron on the results. Subjoined is a table showing the amount of nitrates found in five waters of very different character by the two processes.

Nitrogen in Parts per 100,000.

Sample.	Phenol sulphuric acid.	Carbazol.
1	0·025	0·0247
2	0·050	0·045
3	0·200	0·209
4	1·400	1·38
5	1·600	1·65

THE IODINE ABSORPTION OF ESSENTIAL OILS.

By ROWLAND WILLIAMS, F.I.C., F.C.S.

In the Chemical News (vol. lx., pp. 236 and 245) there appeared two communications—one from Mr. R. A. Cripps, the other from Mr. H. W. Snow—with reference to certain results which I published in the Chemical News (vol. lx., p. 175) in connection with the iodine absorption of essential oils. I should like to make a few observations in reply to the above.

Mr. Snow had already been kind enough to send me (through the courtesy of the Editor of the Chemical News) cuttings from *The New Idea* containing the results of the investigation mentioned in his letter, for which I beg to thank him. I regret having overlooked the work previously done by Messrs. Davies and Snow in this direction, when searching the literature of the subject, as I was most anxious to compare my results with those of other observers. I quite endorse Mr. Snow's statement that determination of the iodine absorption of essential oils is likely to prove extremely useful as an indication of their purity or otherwise. The test must, of

course, be performed under certain specified conditions, or the results obtained will be altogether misleading, but the same may be said of many other well-known analytical processes.

When I was engaged upon the investigation in question, it seemed to me preferable to allow the chloroformic solution of the various essential oils to remain in contact with Hübl's reagent for four hours, that being, I believe, the period of digestion adopted by most analysts in the case of fixed oils and fats. I was aware of the fact that the iodine absorption of many essential oils is incomplete in four hours, but the same remark frequently applies even when the digestion is permitted to go on for the length of time recommended by Mr. Davies, viz., eighteen hours. This point is well brought out in some of the results quoted by Mr. Snow in his original paper. As a case in point, I may also call attention to a sample of oil of peppermint which I examined last week. I found the iodine absorption, under varying conditions, to be as follows :—

Hours.	Per cent.
4	46
6	46
24	67
48	102

If necessary, I could give numerous instances where a distinct advantage is gained by allowing the iodine absorption to proceed for only four hours, instead of eighteen hours or longer. Take, for example, an oil of peppermint adulterated with turpentine. The iodine absorption of genuine oil of peppermint being rather low in four hours, while, on the other hand, turpentine (which has a very high iodine absorbing power) takes up almost its full amount of iodine in that time, it is obvious that if the reaction were allowed to proceed for, say, eighteen hours, the detection of a small proportion of turpentine would be rendered more difficult, owing to the fact that any increase in the iodine absorption would be mainly due to the oil of peppermint, and only slightly due to the adulterant.

In some cases, however, it would probably be useful to determine the iodine absorption in eighteen hours as well as in four hours.

When we remember the widely different conditions under which Mr. Davies and I worked, the fairly close agreement between many of our results is, I think, remarkable. In the case of the oils of bergamot, caraway, and lemon, our respective figures were as follows :—

	Davies.	Williams.
Bergamot	276·1	247·9, 283·7
Caraway	254·9	258·3, *263·2
Lemon	†344·5	320·16, 322·96

There can, I think, be no reasonable doubt that had my determinations been permitted to stand for eighteen hours there would have been even greater concordance between all our figures. I shall take the first convenient opportunity of repeating the iodine absorption during eighteen hours of all the essential oils which I have at hand, in order to satisfy myself on this point.

I ought, perhaps, to call attention to the fact that as the iodine absorption of most essential oils is very high, compared with that of the fixed oils, it is only to be expected that somewhat greater discrepancies will occur between different samples of the former than between those of the latter. Nevertheless, I feel confident that determination of the iodine absorption will frequently be found useful in the examination of essential oils for the numerous adulterants to which they are peculiarly liable.

Laboratory and Assay Office,
28, Pall Mall, Manchester,
November 19, 1889.

* Wrongly quoted by Mr. Cripps as 463·2
† Average of seven samples.

A SOURCE OF ERROR IN SEPARATING SMALL QUANTITIES OF MANGANESE FROM A LARGE QUANTITY OF LIME BY AMMONIUM SULPHIDE.

By L. BLUM.

In precipitating manganese by ammonium sulphide, R. Fresenius proposes to allow in all cases the lapse of at least twenty-four hours, but, in very dilute solutions, forty-eight hours before filtering.

In the analysis of Luxemburg blast-furnace slags, where small quantities of manganese have to be determined in presence of much lime, and in consequence large weights have to be taken for analysis, it has occurred to the writer that in allowing the solution, reduced to a small volume, to stand for some time, there was separated out along with the manganese sulphide another crystalline compound, which rendered the results too high.

The compound was obtained pure by allowing a concentrated solution of calcium chloride mixed with yellow ammonium sulphide to stand for some time, with access of air. The compound separated out in crystals, which adhered firmly to the glass. A qualitative examination showed that it was calcium hyposulphite.

In those cases, therefore, where, in consequence of the co-existence of a little manganese and much lime, a strong concentration of the liquid is requisite, it seems not advisable to allow the precipitate to settle too long. It is then better to proceed according to the process given by Finkener, who filters off the precipitate of manganese sulphide at once after a good ebullition and the addition of a further dose of ammonium sulphide. On proceeding in this manner a deposit of calcium hyposulphite has never been observed.—*Zeitschrift f. Analyt. Chemie*, Part iv., p. 454.

ELECTROLYTIC SEPARATIONS.

By EDGAR F. SMITH and LEE K. FRANKEL.

I. *Separation of Cadmium from Copper.*

The results obtained in the electrolysis of cyanide solutions of mercury and copper, as well as the knowledge gained from our experiments in separating cadmium from zinc, induced us to try whether it would be possible to effect the evaporation of cadmium from copper in cyanide solution. The only electrolytic method proposed for the separation of these metals is that recommended by Smith (*Am. Chem. Journal*, ii., 42), in which solutions con-

Cadmium present. Grm.	Cu present. Per cent.	Cadmium found.
	I.	
0·2426	50	0·2420
	II.	
0·2318	50	0·2331
	50	0·2309
	50	0·2315
	III.	
0·1024	100	0·1028
	100	0·1019
	100	0·1020
	100	0·1032
	100	0·1033
	100	0·1034
	100	0·1014
	IV.	
0·2046	100	0·2034

taining a definite amount of free nitric acid were employed. We experienced no difficulty in making a complete separation, after ascertaining the proper current strength. The conditions most favourable for the separation were essentially the same as those recorded in our former papers, viz.: a dilution of 200 c.c.; 5·5 grms. of potassium cyanide in each experiment, and a current generating 0·28 c.c. oxy-hydrogen gas per minute. Time, sixteen to twenty hours. The results obtained were as in Table.

Copper was not found in any of the deposited cadmium, nor did we discover any of the latter metal in the filtrate containing the copper. The cadmium deposit invariably showed the grey colour characteristic of it.

II. *Action of the Current upon Metallic Sulphocyanides.*

It is well known that in the electrolysis of the sulphate or nitrate of manganese, the oxide of this metal separates upon the positive pole. We have found that if an excess of potassium sulphocyanide be present no such deposition occurs, but, on the contrary, the metal itself will separate as a greyish white, compact deposit upon the negative pole or the vessel attached to it. The addition of a sulphocyanide to the manganese solution undergoing electrolysis, after the oxide has already separated, will cause the solution of the latter. The current necessary for the deposition of metallic manganese, under the conditions mentioned above, should be feeble. The metallic deposit is inclined to rapidly oxidise, and whether manganese can be successfully determined in a quantitative way after this manner will depend very much upon whether we can prevent its oxidation during the drying process.

Nickel, cobalt, iron, and several other metals separate very rapidly from cold sulphocyanide solutions under the influence of a weak current.—*Journal of the Franklin Institute*, August, 1889.

SOME CONSIDERATIONS IN REGARD TO THE FORMATION OF COAL AND CARBONACEOUS MINERALS.

By W. A. DIXON, F.I.C., F.C.S,
Lecturer on Chemistry, Sydney Technical College.

In most chemical manuals the production of coal and similar carbonaceous minerals from cellulose is assumed, and equations are given, showing its transformation into coal of different varieties by the elimination of oxygen and hydrogen as water, carbon and oxygen as carbon dioxide, and carbon and hydrogen as methane. These are known to be evolved during the decomposition of vegetable matter, and are assumed to be given off by cellulose, and as this has a high molecular weight, and as any acquired number of molecules may be used, the equations look very pretty. One can subtract any acquired number of molecules of CO_2H_2O and CH_4 from $C_6H_{10}O_5$, or a multiple of it, and obtain a residue corresponding to anything, from free carbon to cellulose itself. These views are again set forth in one of the latest chemical works bearing on the subject, viz., "Wanklyn's Gas Engineers' Chemical Manual." In connection with this I would point out that in most coals the woody fibre, which contains the greater portion of the cellulose in modern plants, is represented by almost pure carbon, forming the so-called "mother-of-coal," or mineral charcoal. As cellulose was so converted, it is an untenable position that other portions of the *same* substance should, under the *same* conditions, be converted into bituminous matter.

On the other hand, mineralogists and geologists generally lay great stress on the conditions under which the deposit of coal was formed, and refer particular varieties to different horizons as a reason for their different composition and properties. This can be made to agree with the chemical hypothesis mentioned, as it may be said that different quantities of the products would be formed under varying conditions.

There are others who acknowledge that there are at least three conditions which modify the composition of the mineral. Thus, Percy recognises the fact that difference in the composition of vegetable matter due to resinous bodies, &c., may, by increasing resistance to decomposition, tend to preserve vegetable structure ("Fuel," p. 270). Dana says "Coals were once beds of vegetation, analogous in most respects to the peat beds of modern times" ("Mineralogy," p. 758), and on the succeeding page, "between excluded air and imperfectly excluded, and of pressure from heavy superincumbent earthy beds and little or no pressure lie the conditions which attended the origin of the various kinds of coal, and determined, in *connection with the nature of the vegetation itself*, their transformation in progress." From various observations the writer has come to the conclusion that the words put in italics by himself are of more importance than is usually assumed, and that this idea is probably the most important of all. This condition is placed first in a sentence in Ronalds and Richardson's "Knapp's Technology" (i., p. 765), where it says:—"The varieties of coal may depend on the nature of the plants that composed it, the varied circumstances attending their deposit, or the varied conditions under which the beds have subsequently been placed."

My thoughts were first directed to the probable comparatively great importance of the original composition of the plants through examining a number of brown coals from New Zealand, Victoria, Western Australia, and New South Wales, and which I found could be divided into four classes.

1st. Those containing fossil resin (retinite) distributed through them in grains from the size of pin-heads to that of marbles, and amounting sometimes to 20 or 25 per cent of the mass.
2nd. Those containing iron pyrites but no retinite.
3rd. Those containing neither retinite nor pyrites, but having much sulphur in organic combination.
4th. Those without retinite, pyrites, or much sulphur.

Subjected to distillation, the first and last evolved but little sulphuretted hydrogen, the second evolved much of this gas under the conditions of high temperature, the third both at high and low temperature.

If we consider these varieties of imperfect coal it appears probable that, had they been subjected to conditions such as would convert them into coal, the results would be very different for each, although the conditions were the same. The first is evidently produced from highly resinous vegetation, and would probably yield bituminous coal, and the resin gives an aromatic odoured distillate on quickly heating, but the amount of resin available was too small to go into the matter of the products. The second, from non-resinous vegetation, the pyrites being formed by infiltration, would yield a coal like the stinking coal of Lancashire or the brassy coal of some of the Scotch mines. The third it seems probable was produced from vegetation containing much sulphur, such as we find in our modern Cruciferæ, and to this I know of no corresponding true coals. The fourth would correspond to the splint, cherry, and other less bituminous coals.

Again, the deposit of kerosene shale or torbanite at Joadja Creek consists of three distinct layers, separated by almost imperceptible partings, and yet everywhere perfectly distinct. The seam is composed of, first, a layer of splint coal containing a rather large proportion of ash, second, a layer of shale, covered, third, by a layer of bituminous coal of fair quality. In this case it appears that the three layers were deposited in orderly succession, and that all must have been subjected to the same conditions since deposition, and yet the ultimate products are entirely different. It may be observed, in passing, that these

deposits of torbanite, both in New South Wales and Scotland, where one only has been found, seem to have been originally laid down in irregularly lenticular depressions, and observation has indicated that they have never been subjected to excessive pressure, as wherever the "cover" exceeds two or three hundred feet the torbanite is found changed into a carbonaceous slaty mass. It is evident that the differences in the three layers in this seam cannot be ascribed to any other causes than an originally radical difference in the vegetation forming them. Torbanite, Boghead, or kerosene shale, has been legally classed as coal, and it is usually classed with cannels although it is very different. Thus Wanklyn (*loc. cit.*) says—"The following is an analysis of one of the richest cannels, viz., Boghead" (the original torbanite of Scotland). "The large proportion of mineral matter (21 to 22 per cent) will not escape notice; and it will be perceived that Boghead consists of mineral matter saturated with a hydrocarbon containing a larger proportion of hydrogen than there is in benzine, C_6H_6." At Joadja Creek the mineral matter falls as low as six per cent, and it is difficult, I should say impossible, to think of six parts of mineral matter "saturated" with ninety-four parts of hydrocarbon, whilst the overlying coal and sandstone and the underlying coal and sandstone are absolutely free from it.

The old alchemists used to subject everything organic to distinctive distillation, and divide it into water, phlegm, and caput mortuum, and perhaps some information may be gleamed from this industry as now carried out on a large scale. This information is, however, not very direct, owing to the effect of varying temperatures in process, so that the subject is divided into two, namely, high temperature distillation, *i.e.*, gas-making, and low temperature, *i.e.*, oil-making. In the first the liquid and solid hydrocarbons obtained are mostly composed of the aromatic series, whilst those of the latter belong to the fatty series. The gaseous products may be disregarded in both cases, as they are similar, being hydrogen, methane, and some of the lower olefines, and mixed, in the case of high temperature work, with the vapours of aromatic hydrocarbons held in gaseous solution.

In all high temperature work more gas is produced than in low, and carbon is deposited whilst aromatic hydrocarbons are formed, as benzol from polymerisation of acetylene below a red heat, and its conversion by elimination of hydrogen into naphthalene at a red heat, whatever the source of the original hydrocarbon. If, however, we look at what is done commercially with various coals and shales, we shall find that they are not used indiscriminately, but some for one purpose, some for another, according to the value of the products. The statements sometimes found in books are often rather confusing; thus, Knapp says:—"When submitted to destructive distillation all varieties of coal yield the same solid, liquid, and gaseous products, consisting of coke, tar, ammoniacal liquor, benzol, naphtha, naphthaline, paraffin, paraffin oil, and illuminating gas, the proportions of which vary with the quality of the coal and the temperature employed" (Ronalds and Richardson's "Knapp's Technology," vol. i., p. 273). Later writers recognise some difference; thus, Mills says:—"Cannel tars are poorer in aromatic compounds than are bituminous tars" ("Manualette of Destructive Distillation"), and Lunge:—"We may say generally that the tars from peat, brown coal, and bituminous shale consist principally of hydrocarbons of the 'fatty series,' wood-tar of phenols and their derivatives, coal-tar of aromatic hydrocarbons" ("Distillation of Coal-Tar," p. 3). Again:—"Brown coal-tar, as well as that obtained from peat and bituminous shale (and ormerly from the Torbane Hill mineral) is manufactured for its own sake as a principal product, and forms the basis of the West European manufacture of mineral oils and paraffin. The other products of the destructive distillation of such more recent fossils possess very little or no value, except in the case of some very dense coal-like brown coals, which furnish good coke and good gas, but no mineral oil."

These quotations show the general drift of opinion amongst those intimately connected with the subject of distillation, as I have also been more or less for thirty years. There is a radical difference in the substances submitted to retorting, and although the fatty hydrocarbons are more or less converted into gas and aromatic hydrocarbons by a high temperature, the transformation is always incomplete, and I believe that the difference in products arises chiefly from the original differences of the vegetation of which the coal or shale was formed. Of the various mineral fuels, some, as anthracite and splint and cherry coals, are never distilled, the products being of no value. Cokeing coals (in contradistinction to gas-coals which are used for making both gas and coke) are distilled for the sake of the coke, and a few years since it was anticipated that great results would be obtained by the use of Simon Carvés and other improved ovens by which the tar could be collected, but valuable aromatic hydrocarbons were present in such small proportion that the anticipations were not realised. Bituminous gas-coal yields tar rich in benzine, anthracene, and other valuable aromatic hydrocarbons, and practically none of the fatty series, and tar distillers object to the use of shale along with it, as they introduce these.

(To be continued).

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

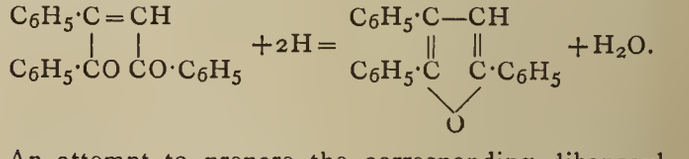
Ordinary Meeting, November 7th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

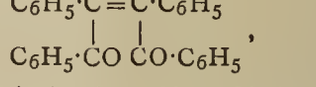
(Concluded fom p. 255).

92. "*αβ-Dibenzoylstyrolene and the Constitution of Zinin's Lepiden Derivatives.*" By Francis R. Japp, F.R.S., and Felix Klingemann, Ph.D.

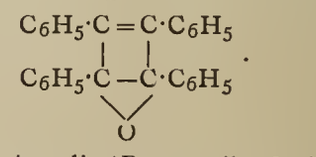
In a preliminary note (*Ber.*, xxi., 2933) the authors showed that by the action of iodhydric acid on *αβ*-dibenzoylstyrolene (anhydracetophenonebenzyl) triphenylfurfuran was formed:—



An attempt to prepare the corresponding dibenzoylstilbene,—



in order to convert it by the action of iodhydric acid into tetraphenylfurfuran, failed; but the authors pointed out (*Ber.*, xxi., p. 2934, footnote) that possibly Zinin's lepiden, $C_{28}H_{20}O$ (m. p. 175°), was the desired tetraphenylfurfuran. In making this suggestion it had escaped their notice that a similar idea had been put forward by Dorn as early as 1870 (*Annalen*, cliii., 358), Dorn calling lepiden "oxyphenyltetrol," and ascribing to it the formula—



Magnanini and Angeli (*Ber.*, xxii., 853) have since found that Zinin's hydro-oxylepiden is identical with Knoevenagel's bidesyl,—

$$C_6H_5\cdot CH—CH\cdot C_6H_5$$
$$\quad\;|\quad\;|$$
$$C_6H_5\cdot CO \quad CO\cdot C_6H_5\ ;$$

and by the dehydrating action of chlorhydric acid they have converted bidesyl into tetraphenylfurfuran identical with lepiden. They regard Zinin's oxylepiden, $C_{28}H_{20}O_2$, as having the formula of the before-mentioned dibenzoylstilbene. This view would make oxylepiden a strict analogue of dibenzoylstyrolene: as dibenzoylstilbene it is phenyldibenzoylstyrolene.

The authors have been engaged for some time in studying the interactions of dibenzoylstyrolene, and find, in support of the foregoing view, that there is an almost perfect parallelism in behaviour between it and oxylepiden. The various compounds obtained by them stand to the corresponding compounds of the lepiden series in the relation of triphenyl-derivatives to tetraphenyl-derivatives, a relation which is exhibited, in the first place, in the case of dibenzoylstyrolene and oxylepiden themselves. It is necessary to point out, however, that of the three "oxylepidens" prepared by Zinin, the analogue of dibenzoylstyrolene is "acicular oxylepiden" (m. p. 220°).

By heating "acicular oxylepiden" with iodhydric acid, Berlin (*Annalen*, cliii., 131) converted it into lepiden (tetraphenylfurfuran). As already mentioned, the authors have shown that when subjected to the same treatment dibenzoylstyrolene yields triphenylfurfuran.

By heating "acicular oxylepiden" Zinin obtained two isomeric "oxylepidens:" as chief product "tabular oxylepiden" (m. p. 136°), and in small quantity "octahedral oxylepiden" (m. p. 232°). In like manner, by heating dibenzoylstyrolene, the authors have converted it into two isomerides: a compound formed in large quantity, crystallising from alcohol in long, lustrous needles, melting at 117—118°, corresponding with "tabular oxylepiden;" and a compound formed only in small quantity, crystallising from alcohol, in which it is very sparingly soluble, in slender white needles, melting at 197—198°, corresponding with "octahedral oxylepiden." They regard the compound melting at 117—118° as *triphenylcrotolactone*, and "tabular oxylepiden" as *tetraphenylcrotolactone*—

$$(C_6H_5)_2C—CH$$
$$\quad\;|\quad\;\|$$
$$\quad CO\ C\cdot C_6H_5$$
$$\quad\;\diagdown\;/$$
$$\quad\;\;O$$

Compound melting at 117—118°.

$$(C_6H_5)_2C—C\cdot C_6H_5$$
$$\quad\;|\quad\;\|$$
$$\quad CO\ C\cdot C_6H_5$$
$$\quad\;\diagdown\;/$$
$$\quad\;\;O$$

"Tabular oxylepiden."

On oxidation with excess of chromic anhydride, triphenylcrotolactone yields benzophenone and benzoic acid. Zinin does not appear to have oxidised "tabular oxylepiden," but he obtained benzophenone from isolepiden, which is formed from "tabular oxylepiden" by distillation.

Caustic potash in alcoholic solution converts triphenylcrotolactone into a salt of *α-diphenyl-β-benzoylpropionic acid*. Zinin has shown that "tabular oxylepiden" yields oxylepidenic acid, $C_{28}H_{22}O_3$, when similarly treated. The following formulæ express the authors' views as to the constitution of these two acids:—

$$(C_6H_5)_2C———CH_2$$
$$\quad\;|\quad\;\;|$$
$$COOH\ CO\cdot C_6H_5$$

α-Diphenyl-β-benzoylpropionic acid (m. p. 182—183°).

$$(C_6H_5)_2C———CH\cdot C_6H_5$$
$$\quad\;|\quad\;\;|$$
$$COOH\ CO\cdot C_6H_5$$

Oxylepidenic acid.

Diphenylbenzoylpropionic acid displays the behaviour of lævulic acid and other γ-ketonic acids. Thus it interacts with phenylhydrazine with elimination of *two* mols. of water, yielding the compound $C_{28}H_{22}N_2O$ (m. p. 185°). In a similar manner hydroxylamine converts it into the compound $C_{22}H_{17}NO_2$, melting at 150—152°. Nascent hydrogen reduces it to a γ-hydroxy-acid, which is very unstable, and when liberated from its salts speedily parts with water, yielding a lactone—

$$(C_6H_5)_2C———CH_2$$
$$\quad\;|\quad\;\;|$$
$$COOH\ CH(OH)\cdot C_6H_5 \;=$$

Triphenyl-γ-hydroxybutyric acid.

$$(C_6H_5)_2C—CH_2$$
$$\quad\;|\quad\;|$$
$$= \quad CO\ CH\cdot C_6H_5 \;+H_2O.$$
$$\quad\;\diagdown\;/$$
$$\quad\;\;O$$

Triphenylbutyrolactone (m. p. 153°).

This lactone may also be obtained directly from triphenylcrotolactone by boiling it with iodhydric acid.

When heated above its melting-point, diphenylbenzoylpropionic acid is re-converted with loss of water into triphenylcrotolactone, a process which corresponds with the formation of the anhydrides of lævulic acid observed by Wolff (*Annalen*, ccxxix., 249). Zinin has shown that oxylepidenic acid can be re-converted by the dehydrating action of heat into "tabular oxylepiden."

Zinin's "octahedral oxylepiden" and the corresponding compound melting at 197—198°, obtained from dibenzoylstyrolene, are difficult to prepare in quantity, and have not yet been fully examined; but the authors incline to the view that these compounds are stereometric isomerides of "acicular oxylepiden" and *αβ*-dibenzoylstyrolene respectively, and would classify them as follows:—

Maleoid Form.	*Fumaroid Form.*
"Acicular oxylepiden." *αβ*-Dibenzoylstyrolene (m. p. 129°).	"Octahedral oxylepiden." Iso-*αβ*-dibenzoylstyrolene (m. p. 197—198°).

By distilling oxylepiden Zinin obtained from it a compound which he called *isolepiden*, assigning to it the formula $C_{28}H_{20}O$, whilst from the mother-liquors from this substance he obtained, by the action of potash, an acid of the formula $C_{28}H_{22}O_3$, to which he gave the name *isoxylepidenic acid*. The authors, therefore, following this analogy, distilled dibenzoylstyrolene, expecting to obtain from it isomerides of triphenylfurfuran and diphenylbenzoylpropionic acid respectively, but found that dibenzoylstyrolene was converted, with evolution of carbon monoxide, into a compound of the formula—

$$C_{21}H_{16}O = C_{22}H_{16}O_2 - CO,$$

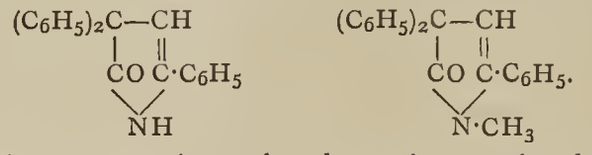
which formed lustrous yellow crystals melting at 92—93°; whilst by the action of potash on the mother-liquors from this compound only ordinary diphenylbenzoylpropionic acid was obtained. As these results were in contradiction to the strict analogy elsewhere observable in the two sets of compounds, they repeated Zinin's experiment on the distillation of oxylepiden, and found that the so-called isolepiden is formed, not by a process of deoxidation, as represented by Zinin, but with elimination of carbon monoxide, $C_{28}H_{20}O_2 = C_{27}H_{20}O + CO$, and is therefore not an isomeride of lepiden at all. The formulæ of the various hydro-"isolepidens" and oxy-"isolepidens" described by Zinin must also, therefore, be correspondingly modified.

From the mother-liquors from the compound $C_{27}H_{20}O$ the authors have obtained the so-called "isoxylepidenic acid," which proves, however, to be not isomeric, as stated by Zinin, but identical with oxylepidenic acid. The "acicular oxylepiden" is converted, during the heating, into "tabular oxylepiden," the greater part of which parts with carbonic oxide, forming "isolepiden," but a small portion distils unchanged and is hydrolysed in the subsequent treatment with alkali, yielding oxylepidenic acid. The analogy is, therefore, preserved also in this case.

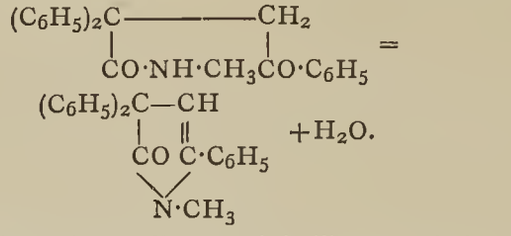
The remaining interactions of dibenzoylstyrolene described in this note have not yet been studied in the lepiden series.

By acting on dibenzoylstyrolene with ammonia the authors obtained (*Ber.*, xxi., 2936) two compounds of the formula $C_{22}H_{17}NO$: one melting at 180°, formed by

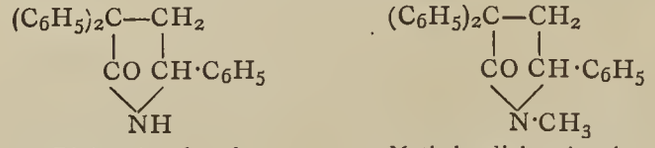
mixing a warm solution of dibenzoylstyrolene with alcoholic ammonia: the second, melting at 221°, formed from the first by long boiling of its solutions, or by heating it alone. They now find that the various primary paraffinoid amines yield similar compounds. As yet only the compound formed with methylamine has been more fully investigated. This compound, which has the formula $C_{22}H_{16}(CH_3)NO$ and melts at 138—139°, and the ammonia compound $C_{22}H_{17}NO$, melting at 221°, can also be very readily obtained by the action of methylamine and ammonia respectively on triphenylcrotolactone. The ammonia compound stands to the methylamine compound in the relation expressed by the following formulæ:—



Adopting a nomenclature based on that employed by Tafel (*Ber.*, xxii., 1861), these compounds would be called 3-*diphenyl*-5-*phenylpyrrholone* and 1-*methyl*-3-*diphenyl*-5-*phenylpyrrholone*; "pyrrholone" being equivalent to "ketopyrrholine," using "pyrrholine" in the generally accepted sense of "dihydropyrrhole." The latter compound may be obtained from triphenylcrotolactone and methylamine in two stages: in the first, the methylamine of diphenylbenzoylpropionic acid is formed; this, on heating, parts with water, yielding the compound $C_{22}H_{16}(CH_3)NO$—



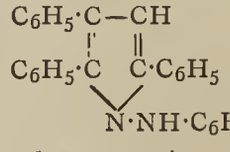
On reduction with sodium and boiling amyl alcohol, these pyrrholones yield the corresponding dihydro-compounds or *pyrrholidones* — derivatives of tetrahydropyrrhole—



3-Diphenyl-5-phenylpyrrholidone (m. p. 201°). 1-Methyl-3-diphenyl-5-phenylpyrrholidone (m. p. 153·5°).

The pyrrholones in question also yield characteristic oxidation products and bromine-derivatives, which are still under investigation, as are also some remarkable cases of isomerism which the authors have discovered among the compounds formed by the action of alkylamines on dibenzoylstyrolene.

By the action of phenylhydrazine on dibenzoylstyrolene, Japp and Huntly obtained (*Trans.*, 1888, 184) a compound of the formula $C_{28}H_{22}N_2$. The authors regard this as most probably an anilidotriphenylpyrrhole, of the constitution—



(*cf.* also Knorr, *Annalen*, ccxxxvi., 295). From the products of the same reaction they have isolated two further compounds; a substance, $C_{28}H_{22}N_2O$, melting at 173—174°, which is apparently a monohydrazone of dibenzoylstyrolene; and a second compound, $C_{21}H_{16}N_2$, melting at 206°, formed by the action of the phenylhydrazine with elimination of a benzoyl-group from dibenzoylstyrolene; this appears to be a *triphenylpyrazole*, isomeric with Knorr and Laubmann's 1-3-5-triphenylpyrazole.

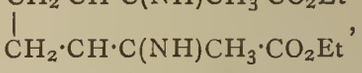
With hydroxylamine hydrochloride, dibenzoylstyrolene yields a compound, $C_{15}H_{11}NO$, melting at 73—75°. Like the foregoing phenylhydrazine derivative, with which it corresponds, it is formed with elimination of a benzoyl-group.

93. "*Ethylic $\alpha\alpha_1$-diacetyladipate.*" By W. H. Perkin, Jun., Ph.D.

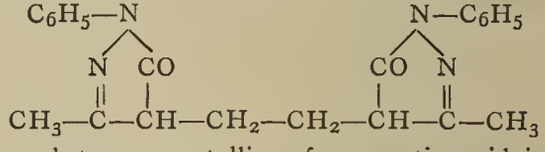
Ethylene bromide and ethylic sodacetoacetate interact readily when heated together in alcoholic solution, forming ethylic acetyltrimethylenecarboxylate and ethylic $\alpha\alpha_1$-diacetyladipate,—

These two substances may be readily separated by distillation in steam, the former passing over with the steam; the diacetyladipate may be extracted from the residue by ether, and is best purified by conversion into the crystalline diimido-compound, which is then hydrolysed by chlorhydric acid. Ethylic diacetyladipate is a thick colourless oil, which gives with ferric chloride a fine violet colouration. On the addition of sodium ethylate to an ethereal solution, a yellowish white precipitate of its disodium derivative is produced, which is readily re-converted by acids into ethylic diacetyladipate.

Ethylic diimidodiacetyladipate,—

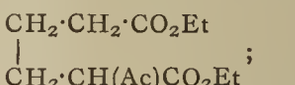


separates from the solution of the ethereal salt in alcoholic ammonia in beautiful colourless plates, which melt at 170°. It readily dissolves in cold dilute acids, but on warming, decomposition into ethylic diacetyladipate and ammonia readily takes place. The corresponding *ethylic diphenylhydrazinediacetyladipate* is formed when ethylic diacetyladipate is warmed with excess of phenylhydrazine. It crystallises from alcohol in light yellow plates, which, when heated above their melting point (145°) are converted into *bis-phenylmethylmethylenepyrazolone*,—

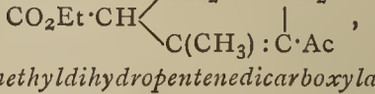


This substance crystallises from acetic acid in small prismatic needles, which do not melt at 250°. It is difficultly soluble in most of the ordinary solvents, but readily soluble in acids and alkalies.

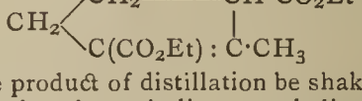
When subjected to distillation under reduced pressure ethylic diacetyladipate yields a yellowish oily distillate, which appears to consist for the most part of three substances, all of which boil approximately at the same temperature (210—225° under 170 m.m.), viz., *ethylic acetyladipate*,—



ethylic methyldihydropentenemethylketonecarboxylate,—



and *ethylic methyldihydropentenedicarboxylate*,—



If the crude product of distillation be shaken with dilute aqueous potash, the ethylic acetyladipate dissolves, forming an acid ethereal salt, which, on distillation, is decomposed into carbon dioxide and ethylic ω-acetylvalerianate, a colourless oil boiling at 200—205° (150 m.m.). *ω-Acetovalerianic acid*, which is readily obtained

from the ethereal salt by hydrolysis, forms a crystalline mass which melts at 40—42°, and distils at 250—253° (280 m.m.) with slight decomposition.

The residual oily product of distillation of ethylic diacetyladipate, which is insoluble in potassium hydrate, yields on hydrolysis two principal products. One of these is a neutral substance, $C_8H_{12}O$, which boils constantly at 191°, and smells strongly of camphor. From its reactions this substance appears to be methyldihydropentenemethylketone,—

$$CH_2\begin{cases}CH_2\cdot CH\cdot CO\cdot CH_3\\ \|\\ CH_2\cdot C\cdot CH_3\end{cases}.$$

It combines readily with hydroxylamine, forming a beautifully crystalline hydroxime, $C_8H_{13}NO$, which melts at 86°; when heated to 100° with Beckmann's reagent (acetic acid, acetic anhydride, and hydrogen chloride) this compound is converted into an isomeric oily substance of pronounced basic properties, which boils at 164—165° and readily dissolves in water, forming a strongly alkaline solution. The platinochloride—

$$(C_8H_{13}NO)H_2PtCl_6$$

crystallises from water in magnificent red prisms.

The second product of hydrolysis, methyldihydropentenedicarboxylic acid, crystallises from water in colourless plates which melt at 188°.

Concentrated sulphuric acid converts ethylic diacetyladipate into a substance of the formula $C_{12}H_{18}O_4$, which appears to be ethylic methyldihydropentene.

94. "(1·2) *Methylethylpentamethylene.*" By T. Rhymer Marshall, D.Sc., and W. H. Perkin, jun., Ph.D.

Ethylic $\alpha\alpha_1$-diacetyladipate when carefully hydrolysed by alcoholic potash yields α-ω-diacetylbutane,—

$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot CO\cdot CH_3.$$

This substance is a white crystalline solid, which melts at 43—44°: it is converted by dehydrating agents, or by boiling with alcoholic potash, into the methyldehydropentenemethylketone described in the previous abstract.

Methylpentamethylenemethylcarbinol,—

$$\begin{array}{l}CH_2\cdot CH_2\\ |\quad\ |\\ CH_2\ CH\cdot CH(OH)\cdot CH_3,\\ \quad\diagdown\diagup\\ \quad\ CH\cdot CH_2\end{array}$$

is obtained by reducing methyldihydropentenemethylketone with sodium in moist ethereal solution. It forms a colourless oil boiling at 181°, smelling strongly of menthol.

The *acetate*, $C_8H_{15}OC_2H_3O$, is readily prepared by boiling the alcohol with acetic anhydride. It boils at 133—135° (90 m.m.), has a smell resembling that of the acetate of the higher alcohols of the fatty series, and is very readily hydrolysed by potash.

The *iodide*, $C_8H_{15}I$, is a colourless oil, boiling at 155—160° (90 m.m.), which has an odour resembling that of amyliodide.

Methylethylpentamethylene,—

$$\begin{array}{l}CH_2\cdot CH_2\\ |\quad\ |\\ CH_2\cdot CH\cdot CH_2\cdot CH_3,\\ \quad\diagdown\diagup\\ \quad\ CH\cdot CH_3\end{array}$$

is produced when the iodide is heated with iodhydric acid and amorphous phosphorus in sealed tubes at 234—240° for eight hours. It is a limpid liquid boiling at 124°, and smelling very like light petroleum. By the reduction of methyldihydropentenemethylketone with sodium in moist ether, a considerable quantity of a secondary product, $C_{16}H_{30}O_2$, is formed, which is a very thick oil boiling at 250—255° (50 m.m.). If sodium amalgam be used as a reducing agent, two substances of complicated composition are formed, *i.e.*, $C_{16}H_{22}O$ (b. p. 220°, 25 m.m. pressure) and $C_{16}H_{24}O_2$ (b. p. 250—260°, 25 m.m. pressure).

95. "*Action of Dehydrating Agents on α-ω-Diacetylpentane. Formation of Methylethylhexamethylene.*" By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, jun., Ph.D.

α-ω-Diacetylpentane, under the influence of dehydrating agents, loses one molecule of water and is converted into a compound of the formula $C_9H_{14}O$; although the constitution of this substance has not yet been proved beyond doubt, its formation and its properties seem to show that it has the constitution of an orthomethyltetrahydrobenzene methylketone (orthomethyacetyltetrahydrobenzene,—

$$CH_2\begin{cases}CH_2\cdot CMe\\ CH_2\cdot CH_2\end{cases}C\cdot COMe.$$

This compound is best prepared by dissolving diacetylpentane in concentrated sulphuric acid. It is a colourless mobile oil, boiling at 205—206°, and smelling strongly of peppermint; it is insoluble in water, but is miscible with alcohol, ether, &c., in all proportions. It is not decomposed when heated with water at 150°, or when treated with 80 per cent sulphuric acid at the ordinary temperature; it does not combine with mercuric chloride.

The *hydroxime*, $C_6H_8Me\cdot CMe{:}NOH$, prepared by treating the ketone with hydroxylamine chlorhydride and excess of potash in alcoholic solution, is a thick, slightly yellow oil, sparingly soluble in hot water, readily in potash and concentrated hydrochloric acid. The *hydrazone*, $C_6H_8Me\cdot CMe{:}N_2Ph$, obtained by heating the ketone at 100° with phenylhydrazine, is a thick yellow oil, which decomposes gradually on exposure to the air.

Orthomethylhexamethylenemethylcarbinol,—

$$CH_2\begin{cases}CH_2\cdot CHMe\\ CH_2-CH_2\end{cases}CH\cdot CHMe\cdot OH,$$

obtained by reducing methyltetrahydrobenzenemethylketone with sodium in moist ethereal solution, is a colourless oil, which boils at 195—200°, and has a smell very like that of menthol. It is insoluble in water, but is miscible with most of the ordinary solvents in all proportions, and it dissolves in concentrated hydriodic acid with evolution of heat,

The *acetate*, $C_6H_{10}Me\cdot CHMe\cdot OAc$, prepared by boiling the alcohol with acetic anhydride, is a colourless liquid boiling at 204—210°.

The *iodide*, $C_6H_{10}Me\cdot CHIMe$, is a heavy colourless liquid boiling at 178—180° (110 m.m.) and possessing a smell exactly like that of amyl iodide.

Orthomethyltetrahydrobenzenemethylcarbinol,—

$$CH_2\begin{cases}CH_2\cdot CMe\\ CH_2\cdot CH_2\end{cases}C\cdot CHMe\cdot OH,$$

is formed in small quantities in the preparation of orthomethylhexamethylenemethylcarbinol when the quantity of sodium employed is insufficient for complete reduction. It is a colourless liquid boiling at 141—143° (50 m.m.).

Orthomethylethylhexamethylene, $C_6H_{10}MeEt$, is obtained when methylhexamethylenemethylcarbinol is heated at 230—240° for four hours with a large excess of hydriodic acid of sp. gr. 1·96 and a little amorphous phosphorus. It is a colourless mobile liquid, with a smell closely resembling that of light petroleum, and boils at 150—152°.

The compound $C_{18}H_{26}O$ is obtained in the preparation of diacetylpentane and is formed by the condensation of two molecules of the diketone with elimination of three molecules of water; it is a very thick yellowish oil boiling at 265—275° (35 m.m.).

A condensation compound, $C_{18}H_{32}O_2$, is formed in the reduction of methyltetrahydrobenzenemethylketone; it is a thick yellowish oil, boiling at 255—265° (50 m.m.).

96. "*Action of Reducing Agents on α-ω-Diacetylpentane Formation of Dimethylheptamethylene.*" By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, jun., Ph.D.

When α-ω-diacetylpentane is treated with excess of

sodium in moist ethereal solution, it is chiefly converted into orthodihydroxydimethylheptamethylene,—

$$CH_2\begin{<}CH_2\cdot CH_2\cdot CMe\cdot OH \\ CH_2\cdot CH_2\cdot CMe\cdot OH\end{>}.$$

The same compound is formed when the diketone is reduced with sodium and alcohol at 80—100°. It is a thick colourless liquid, with a sharp, bitter taste, and a peculiar aromatic smell, rather like that of menthol. It boils at 201—202° (180 m.m.), is volatile with steam, and distils, seemingly without decomposition, at the ordinary temperature when heated in small quantities. It is sparingly soluble in cold water, but separates from the solution on warming or on adding sodium carbonate. It does not combine with sodium, hydrogen sulphite, nor with hydroxylamine in alkaline solution. The sodium-derivative, $C_7H_{10}Me_2(OH)\cdot ONa$, seems to crystallise with 1½ mols. H_2O, and is readily decomposed by water or when gently heated.

Orthodibromodimethylheptamethylene, $C_7H_{10}Br_2Me_2$, is obtained when the dihydroxy-compound is treated with excess of phosphoric bromide in chloroform solution. It is a yellowish mobile liquid, with an unpleasant, very irritating smell, and gradually decomposes on exposure to the air.

The *iodide*, $C_7H_{10}IMe_2\cdot OH$, can be prepared by boiling dihydroxydimethylheptamethylene with hydriodic acid of sp. gr. 1·96. It is a colourless oil, insoluble in water.

The diacetyl-derivative, $C_7H_{10}Me_2(OAc)_2$, prepared by boiling dihydroxydimethylheptamethylene with acetic anhydride, is a colourless mobile liquid, boiling at 199—202° (65 m.m.); it is readily hydrolysed by potash.

Orthodimethylheptamethylene, $C_7H_{12}Me_2$, is obtained, together with considerable quantities of a condensation product, when dihydroxydimethylheptamethylene is heated at 230—250° for eight hours with a large excess of hydriodic acid of sp. gr. 1·96, and a little amorphous phosphorus. It is a colourless mobile oil, boils at 150—152°, and has a smell not to be distinguished from that of light petroleum.

A compound, $C_{18}H_{34}O_3$, is formed in small quantities in the preparation of dihydroxydimethylheptamethylene; it is a very thick yellowish oil, boiling at 300—310° (200 m.m.).

97. "*Oxyamidosulphonates and their Conversion into Hyponitrites.*" By EDWARD DIVERS, M.D., F.R.S., and TAMEMASA HAGA, F.C.S.

The oxamidosulphonates are the sulphazidates of Fremy, which Claus and Raschig have shown to be monosulphonic-derivatives of hydroxylamine. A modification of Fremy's method of preparing the acids has been devised by the authors, dependent on their discovery of the existence of a neutral soluble barium salt in addition to that of the basic salt. They find that the sodium salt can only be prepared as a colourless, very viscid liquid, which does not solidify in the desiccator. The potassium salt is crystalline, but is not anhydrous, as stated by Claus.

The main interest of this paper lies in the behaviour of oxyamidosulphonates with strong alkalies, and with copper hydroxide. On treatment with alkali, instead of yielding sulphate and hydroxylamine, as asserted by Claus and Raschig:—

$$HO\cdot NH\cdot SO_3K + KOH = HONH_2 + K_2SO_4,$$

and as it is admitted they do when hydrolysed by an acid, the authors find that they are converted exclusively into sulphite and hyponitrite, thus—

$$2HO\cdot NH\cdot SO_3K + 4KOH = (KON)_2 + 2K_2SO_3 + 4OH_2;$$

this interaction affords much the most fruitful process known for converting nitrite into hyponitrite.

The reducing action of the sulphazidates was known even to Fremy, and has since been referred to the supposed conversion of the salts into hydroxylamine and sulphate, the hydroxylamine being supposed then to act on the copper hydroxide in the well-known way. The authors find in opposition to this belief that much sulphite as well as sulphate is formed, and that the cupric oxide reduced is only half that calculated on the above supposition. They would write the equation—

$$2HO\cdot NH\cdot SO_3K + 2CuO + 2KOH = \\ = K_2SO_3 + K_2SO_4 + Cu_2O + N_2O + 3H_2O,$$

and hold that it is the undisplaced hydrogen of ammonia only which in the salt acts directly as the reducing agent.

98. "*The Alloys of Lead, Tin, Zinc, and Cadmium.*" By A. P. LAURIE.

In extension of his previous observations (*Trans.*, 1888, p. 88) the author has made voltaic cells with the various alloys and has thus compared their behaviour with that of the single metal by means of an electrometer. He concludes that the metals now examined do not combine together, thus confirming Matthiessen's conclusions.

PHYSICAL SOCIETY.

November 15, 1889.

Prof. REINOLD, F.R.S., President, in the chair.

PROF. J. MILNE and Lieut. G. F. Eyre were elected Members.

Mr. ENRIGHT resumed the reading of his paper on the "*Electrification due to Contact of Gases with Liquids.*" Repeating his experiments with zinc and hydrochloric acid, the author, by passing the gas into an insulated metallic vessel connected with the electrometer, proved that it was always charged with electricity of the opposite kind to that of the solution.

The electrical phenomena of many other reactions have been investigated, with the result that the gas, whether H, CO_2, SO_3, SH_2, or Cl, is always electrified positively when escaping from acids, and negatively when leaving a solution of the salt. In some cases distinct reversal is not obtainable, but all these seem explicable by considering the solubility and power of diffusion of the resulting salts. Various other results given in the paper tend to confirm this hypothesis.

Seeking for an explanation of the observed phenomena, the author could arrive at no satisfactory one excepting "contact" between gases and liquids, and if this be the true explanation, he hoped to prove it directly by passing hydrogen through acid. In this, however, he was unsuccessful, owing, he believes, to the impossibility of bringing the gas into actual contact with the liquid. True contact only seems possible when the gas is in the nascent state. Some difficulty was experienced in obtaining non-electrified gas, for the charge is retained several hours after its production, even if the gas be kept in metallic vessels connected to earth. Such vessels, when recently filled, form condensers in which the electricity pervades an enclosed space, and whose charge is available on allowing the gas to escape. Soap-bubbles blown with newly generated hydrogen were also found to act as condensers, the liquid of which, when broken, exhibited a negative charge. This fact, the author suggested, may explain the so-called "fire-balls" sometimes seen during thunderstorms, for if by any abnormal distribution of heat a quantity of electrified air becomes enclosed by a film of moisture, its movements and behaviour would closely resemble those of fire-balls. A similar explanation was proposed for the phenomenon mentioned in a recent number of *Nature*, where part of a thundercloud was seen to separate from the mass, descend to earth, and rise again.

The latter part of the paper describes methods of measuring the contact potential differences between gases and liquids, the most satisfactory of which is a "water-dropper," and by its means the P.D. between hydrogen and hydrochloric acid was estimated to be about 42 volts.

Prof. RÜCKER asked if the experiment with zinc and hydrochloric acid could be started in the second stage by having the acid partly saturated with salt.

Dr. C. V. BURTON thought it probable that contact could be made between a gas and a liquid by shaking them up together in a bottle.

In reply, Mr. ENRIGHT said the experiment could be started at any stage, and reversal effected as often as desired by adding either acid or a solution of salt to the generating vessel.

Mr. HERBERT TOMLINSON read a paper on the "*Effect of Repeated Heating and Cooling on the Electrical Resistance and Temperature-Coefficient of Annealed Iron.*"

In a paper recently presented to the Royal Society the author has brought forward an instance of an iron wire which, when subjected to magnetic cycles of minute range alternately at 17° and 100° C. had its molecular friction and magnetic permeability reduced respectively to about one-fourth and one-half their original values. The present experiments were undertaken to see whether by such heatings and coolings the temperature-coefficient of iron could be brought down to something approaching the number given by Matthiessen for "most pure metals." The wire experimented on was first annealed by heating to 1000° C. for several hours and allowing to cool slowly in a furnace placed at right angles to the magnetic meridian. The process was repeated three times. Afterwards the wire was covered with paper and wound doubly into a coil. This coil was enclosed in a water-jacketted air-chamber and connected with a sensitive Wheatstone bridge. Thermo-electric and Peltier effects were eliminated by always keeping the galvanometer circuit closed. By repeated heating to 100° C. and cooling to 17° C. for long intervals, the specific resistance at 17° C. was reduced from 11,162 to 10,688 C.G.S. units, after which the operations produced no further change; at the same time the temperature-coefficient increased in the proportion of 1 : 1·024. From careful determinations of the resistance at different temperatures the formula—

$$R_t = R_0(1+0{\cdot}005131t + 0{\cdot}0000081 5t^2)$$

was deduced, whilst that obtained from Matthiessen's results for pure iron annealed in hydrogen is—

$$R_c = R_0(1+0{\cdot}005425\ t+0{\cdot}0000083\ t^2).$$

Taking his own determination of specific resistance of impure iron as correct, coupled with Matthiessen's law connecting the resistances and temperature-coefficients of metals and their alloys, the author finds that the specific resistance of pure iron, deduced from Matthiessen's results, is from 4 to 5 per cent too high.

In conclusion, Mr. Tomlinson expresses a hope that the B.A. Electrical Standards Committee may be induced to determine the absolute resistance and temperature-coefficient of the pure metals which are in ordinary use.

Prof. AYRTON thought Matthiessen's results were expressed in B.A. units, and hence might appear one or two per cent too great. Mr. Tomlinson, however, believed the numbers he took were expressed in legal ohms.

Dr. WALMSLEY asked for what value of the magnetising force the permeability of the iron mentioned in the beginning of the paper was determined.

Mr. TOMLINSON replied that they were much smaller than the earth's horizontal component.

Dr. THOMPSON'S paper on "Geometrical Optics" was postponed.

OBITUARY.

DR. GUSTAVE QUESNEVILLE.

WE much regret having to put on record the death of Dr. Gustave Quesneville, which took place on the 14th inst. at his residence in the Rue de Buci, Paris.

The deceased has long occupied a prominent and honourable place in the scientific journalism of France. In 1840 he founded the *Revue Scientifique*, and conducted it until 1853. In 1857 he established the *Moniteur Scientifique*, which he has since edited, and which now ceases to appear. Our deceased colleague had reached the age of 80 years.

CORRESPONDENCE.

METAMORPHISM OF ROCKS.

To the Editor of the Chemical News.

SIR,—In the appreciative notice of my little work on the "Metamorphism of Rocks," which appeared in the CHEMICAL NEWS (vol. lx., p. 256), there are two points raised on which, in my prefatory note, I have not been quite clear.

1. The "outcry referred to" is not exactly that raised by Mr. A. Herbert's manifesto, with much of which I entirely sympathise, but the clamour for a "teaching university" in London to supersede or supplement the present university, which, so far from deserving much o the censure it has received, is, I think, deserving of more praise for *the* function it has fulfilled in the advancement of higher education in this country, setting up, as it does, a standard at once comprehensive and high for its *pass* degrees, instead of seeking to make itself a mere congeries of "finishing-schools" for young gentlemen.

2. I spoke of the academical career as a "race" *de facto*. It is not merely a "radical error," but the principle which vitiates English education more, perhaps, than anything else. It is one thing, however, to deprecate an evil, quite another thing to cure it; nor do I think there is much hope, for, so long as the present expensiveness of English university life is maintained, and the immoral trafficking in young brains, which underlies the scholarship system from the colleges at the universities down to the small preparatory school-boy of eight or nine, continues.—I am, &c.,

A. IRVING.

Wellington College, Berks,
November 24, 1889.

WATER-BATH REGULATOR,

To the Editor of the Chemical News.

SIR,—It seems to me that the water-bath regulator described in the CHEMICAL NEWS (vol. lx., p. 250), could be made simpler still by doing away with the upper side-tube altogether, and passing the cold water in by the end of the tube figured as being open to the air.—I am, &c.,

"X."

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 19, November 4, 1889.

On Phenyl Thiophene. — Adolphe Renard. — This compound forms brilliant white tablets melting at 170°, easily volatile, boiling about 330°. It is sparingly soluble in cold alcohol, more readily in hot alcohol, very soluble in benzene, petroleum essence, chloroform, carbon disulphide, less soluble in ether. It yields with isatin and sulphuric acid a blue solution, and with phenanthrenequinone and sulphuric acid a green colour. Its composition is expressed by the formula $C_6H_5-C_4H_3S$. If ox-

idised with chromic acid in an acetic solution it gives benzoic acid.

Researches on Digitaline and Tanghinine.— M. Arnaud.—The author assigns to digitaline the formula $C_{31}H_{50}O_{10}$, and to tanghinine $C_{27}H_{40}O_8$.

Bulletin de la Société d'Encouragement pour l'Industrie Nationale. Series 4, Vol. iv., No. 40.

Report presented by H. Le Chatelier on behalf of the Committee of Chemical Arts on M. Candlot's work entitled "Practical Study on Portland Cement." —M. Candlot enumerates as the different methods now employed in the assay of cements:—Chemical analysis, measurement of the degree of fineness, determination of density, rapidity of setting, and determination of resistance to rupture. The composition of good cements does not vary widely. As a specimen of a good cement of average composition he gives:—Silica, 22·20; alumina, 6·72; iron oxide, 2·28; lime, 67·31; magnesia, 0·95; various, 0·66; total, 100·12. Any cement which deviates widely from this composition may be suspected, but one presenting a composition similar to the above is not necessarily good. A proportion of volatile matters (water and carbon dioxide) exceeding 3 per cent indicates an alteration from the action of air involving a decrease of resisting power. Matter insoluble in acids should not reach 1 per cent. An escape of hydrogen sulphide on the addition of an acid often indicates the fraudulent addition of blast-furnace slags. Chemical analysis, therefore, merely enables us to eliminate certain samples of bad quality, but it does not guarantee the good quality of others. *Fineness of Powder.* — The degree of fineness is measured by the quantity which does not pass through sieves of increasing grades of fineness; *e.g.*, No. 50 has 324 meshes per square centimetre, No 8 900, and No 200 5000. The degree of fineness is a useful datum, because granules which are too bulky do not become hydrated within, say, a month, but behave like inert sand. The proportion of grains which do not pass through the sieve of 5000 meshes should be reduced to a minimum. *Density.*—This datum varies widely according as we operate upon a single granule or upon a known volume of the powder. M. Candlot recommends that for determinations of density we should take only the portion which passes through sieves of 5000 meshes. Cements which have been well furnaced give 1·05 to 1·12; those badly furnaced, 0·93 to 1. *Duration of Setting.*—M. Candlot shows that the presence of foreign salts in the water modifies the time of setting. Calcium chloride, sulphate, and nitrate have a retarding influence; sodium chloride is inert. Sea-water has a strongly retarding influence as compared with fresh water. A sample of cement with fresh water set in twenty-five minutes; with sea-water in seven hours and a half; and with a one per cent solution of calcium chloride in ten hours. The rapidity of setting is an element too variable to furnish precise indications of the quality of a cement. M. Candlot considers that a useful cement should have the following properties:—(1) It should, when mixed with a suitable quantity of sand, present a sufficient resistance to a crushing pressure, but this resistance need not necessarily be very high. (2) The cement should possess a sufficient adhesiveness to ordinary building materials—brick and rough calcareous stones. (3) It must not become spontaneously disintegrated, split, or swell up, as occurs with samples containing free lime. (4). It must not become disintegrated under the influence of excessive atmospheric changes, such as dryness of the air or frost. (5) Cement for marine engineering works should resist as long as possible the action of magnesian salts.

Revue Universelle des Mines et de la Metallurgie. Series 3, Vol. vi., No. 1.

Studies on the Processes of Analysis of the Raw Materials and the Products of Siderurgy.—Dr. M. C. Meinecke.—In this article the author speaks of the determination of sulphur in irons. He prefers the processes in which the hydrogen sulphide formed is converted into sulphuric acid by direct oxidation. As an oxidising agent he recommends alkaline oxygenated water, as used by Classen. The metal is dissolved in dilute hydrochloric acid (1 vol. acid at 1·19 sp. gr. and 1 vol. of water) in a flask holding 500 c.c., and connected with a continuous apparatus for generating hydrogen. The delivery-tube passes into a flask holding 250 c.c., in which the acid fumes are condensed and are then conveyed into two Volhard condensers, containing each 50 c.c. of oxygenated water at 2·5 per cent with 10 c.c. soda-lye (1 part pure sodium hydroxide dissolved in 3 parts of water). The metal is dissolved at first in the cold, and finally a gentle heat is applied.

Reduction of Ferric Bromide by Boiling its Solution.—L. L. de Koninck.—The products of the reaction are ferrous bromide and free bromine. The author considers that this reaction should be kept in view in operations where bromide is used as an oxidising agent in presence of iron.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Spermiciatia.—Can any correspondent tell me of a manufacturer in England of "spermiciatia?"—A Constant Reader.

MEETINGS FOR THE WEEK.

Monday, Dec. 2nd.—Medical, 8.30.
—— Royal Institution, 5. General Monthly Meeting.
—— Society of Arts, 8. (Cantor Lectures). "Modern Developments of Bread-making," by William Jago.
Tuesday, 3rd.—Institute of Civil Engineers, 8.
Wednesday, 4th.—Society of Arts, 8. "Rabies and its Prevention," by Armand Ruffer, M.A., M.D.
—— Geological, 8
Thursday, 5th.—Royal, 4.30.
—— Royal Society Club, 6.30.
—— Chemical, 8. Ballot for the Election of Fellows.
Friday, 6th.—Physical, 5. "The Electrification of a Steam Jet," by Shelford Bidwell, F.R.S. "Notes on Geometrical Optics," Part II., by Prof. S. P. Thompson, D.Sc. "On the Behaviour of Steel under Mechanical Stress," by C. H. Caras Wilson. "On a Carbon Deposit in a Blake Telephone Transmitter," by F. B. Hawes.
—— Geologists' Association, 8.

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See opinion *Electrical Review*, October 21.

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THE CHEMICAL NEWS.

Vol. LX. No. 1567.

A NEW, EASY, RAPID, AND CORRECT METHOD OF DETECTING TIN IN MINERALS.

By ALEXANDER JOHNSTONE, F.G.S. (London and Paris).
Assistant to Professor of Geology and Mineralogy in the University of Edinburgh.

Minerals containing tin yield, when mixed with fluxes and properly heated for some time before the blowpipe on charcoal in a good strong reducing flame, malleable metallic globules of a high lustre and silver-white colour. For the reduction of the ores of tin and most of the other minerals known to contain that metal, the common white flux or fusion-mixture of Fresenius ($K_2CO_3 + Na_2CO_3$) is quite adequate. In certain obstinate cases, however, it is advisable to use a little borax or potassium cyanide, or both, as well as fusion mixture. As the tin almost invariably, in the process of ordinary reduction on charcoal, separates out in rather small beads, which, because of their very fluid consistency at the temperature of the blowpipe flame, sink rapidly down through the flux, &c., to the bottom of the assay, or even a little distance into the support, it is necessary to cut out the ignited residue with some of the surrounding carbon on each side and below it, and transfer the whole to a mortar, where, after the operations, first of heavy and firm grinding to reduce the mixture to a fine powdery condition, and then of washing or lixiviating with water in order to remove everything of a non-metallic nature, have been gone through, the silver-like malleable scales of the metal will be observed mainly adhering to the bottom of the mortar, but in part also to the pounding extremity of the pestle.

To prove that these silvery scales are tin, throw over them, in the mortar, two or three drops of boiling concentrated hydrochloric acid, and then add, by means of a glass tube, one drop of a fairly strong water solution of gold chloride and swing the mixture of liquids all round the bottom of the mortar for about a minute. If the white metallic scales originally observed were composed wholly or partially of tin, then, by the treatment described, the bottom of the white porcelain or earthenware mortar will receive a distinct purple stain by the formation of the well-known characteristic purple of Cassius. To further confirm the presence of tin, allow a current of sulphuretted hydrogen gas to impinge for a very short time on the moist stained bottom of the mortar. The formation of a skin of brown stannous sulphide, arising from this action, will afford valuable additional and sufficient confirmation of the presence of the metal.

RATE OF DECOMPOSITION OF CHLORINE-WATER BY LIGHT.*

By Dr. G. GORE, F.R.S.

In this research, the author has investigated, by means of the voltaic balance, the kind and amount of chemical change, the rate at which decomposition proceeds, and the chemical composition of the products formed at all stages of decomposition of chlorine-water when exposed to daylight and sunlight in colourless glass vessels.

The chlorine-water, by exposure to diffused daylight, was decomposed with moderate uniformity, but at a gradually diminishing rate, as shown by the losses of voltaic energy, until no further loss of such energy occurred; the liquid then consisted of an aqueous solution of hydrochloric acid, hydrochlorous acid, and chloric acid. By further exposure of the liquid to daylight and sunlight during several weeks, peroxide of hydrogen was formed, and the amount of hydrochloric acid and voltaic energy very slowly increased until that of the latter became equal to that of dilute hydrochloric acid of equivalent strength to the whole of the chlorine present; all the other chief properties of the final liquid agreed with those of a mixture of dilute hydrochloric acid and peroxide of hydrogen. Still further exposure to strong sunlight caused no further change in chemical composition, amount of voltaic energy, or other property of the liquid.

This research shows distinctly that the decomposition of chlorine-water by light may be divided into two essentially different parts, or periods, of chemical change, and that the kinds of chemical change occurring during these two periods are largely different. During the first period, a very great and gradual *loss* of voltaic energy occurs, attended by formation of hydrochloric, hydrochlorous, and chloric acids. During the second period, a moderate and very slow *increase* of voltaic energy takes place, accompanied by decomposition of the hydrochlorous and chloric acids; a further formation of hydrochloric acid, and the production of peroxide of hydrogen. Under the influence of prolonged sunlight, the whole of the oxygen of the hydrochlorous and chloric acids united with water to form peroxide of hydrogen, and the peroxide then combined with the whole of the hydrochloric acid to form a definite "solution compound," represented by the formula $2HCl.H_2O_2$.

The chemical composition of the products of the change at the end of the first and second periods were ascertained by means of the voltaic balance and ordinary chemical analysis. During the first period, forty consecutive measurements of the voltaic energy, at stated intervals of time, were made, and the energy diminished from about 1219 millions to 2·9 millions; and during the second period, eight such measurements were made, and the energy increased to 9·3 millions. A curve is given showing the rate of loss of energy during the first period.

It is interesting to observe that suitably decomposed chlorine-water, or possibly, in its stead, a mixture of—

$$6HCl + HClO + HClO_3$$

in a proper proportion of water, has the property of absorbing energy by exposure to light, very much like that possessed by the green leaves of plants.

* Abstract of a Paper read before the Royal Society, June 20, 1889.

ON THE PREPARATION OF A STANDARD SOLUTION OF FERRIC SALTS WITHOUT TITRATION,

By WILLIAM FRENCH, A.I.C.

In the course of practical instruction here, I have occasion frequently to prepare standard solutions of ferric salt for subsequent titration by the students; the method employed being previous reduction by Zn and H_2SO_4 and titration with $KMnO_4$.

The ferric salts available for such purpose, as sulphate, are, as a rule, impure and not always soluble, and therefore one has to titrate the solution after weighing the salt in order for the strength to be known. It occurred to me, however, to take a weighed quantity of ferrous ammonium sulphate, which can be obtained in a state of purity, dissolve in water, add a little sulphuric acid, and then hydrogen dioxide in small quantity; warm up, and finally boil, to expel excess of oxygen and decompose traces of H_2O_2.

I find this method works admirably, and the solution so obtained can be relied on as containing the iron put in, in

the ferric state, and needs no standardisation. The whole operation takes about half an hour.

University Chemical Laboratory,
Cambridge.

DETERMINATION OF TUNGSTEN IN METALLIC TUNGSTEN.

By ALFRED ZIEGLER.

In the *Chemiker Zeitung*, 1889, No. 36, is given a process by J. Preusser, which much abridges the determination of tungsten. He roasts the sifted metal in contact with air, and treats subsequently with aqua regia and hydrochloric acid, &c. The roasting, however, lasts for some hours, and cannot be executed in a platinum crucible, since tungsten attacks platinum, probably forming an alloy. It even leaves upon porcelain a permanent spot, perhaps imponderable, but enough to offend the eye of a conscientious chemist.

The author has succeeded in completing the roasting of tungsten in about three-quarters of an hour, as follows:—½ grm. of tungsten, finely ground in an agate mortar, is thrown upon ammonium nitrate melting at a low temperature in a platinum crucible (the ammonium salt must have been previously dehydrated by fusion). It is then heated until all the nitrate is driven off, leaving in the crucible the superficially oxidised metal, which, without injuring the crucible or the result, can be completely oxidised in a short time with a full Bunsen flame, stirring carefully with a stout platinum wire. The rest of the analysis is conducted in the usual manner.—*Chemiker Zeitung*.

ON THE QUALITATIVE ANALYSIS OF THE AMMONIUM SULPHIDE PRECIPITATE.

By F. MAYER.

In the first practical exercises in the laboratory it is well known that the separation of the ammonium sulphide precipitate presents various difficulties for the beginner.

Among the methods for examining this precipitate, separation with sodium acetate has been recently recommended as the simplest. This process rests upon the fact that, on boiling with sodium acetate, ferric oxide, and alumina in solutions as completely neutralised as possible are deposited respectively as basic acetate or as hydroxide, whilst salts of manganese and zinc remain in solution (nickel and cobalt are supposed to have been previously eliminated). In the absence of chromium compounds this separation, with due care, may be accurately and speedily effected; but not so in its presence, since chromium oxide by itself is not precipitated by boiling with sodium acetate, but in presence of ferric oxide it is sometimes precipitated and sometimes not, and occasionally it prevents the complete precipitation of the iron. The phenomena are similar to those which occur on adding potassium hydroxide to mixed solutions of ferric and chromic oxides.

From such solutions, however, ferric oxide and chromic oxide may be thrown down quantitatively by potassa if the former oxide is in excess as compared with the second (say 4 : 1). It seemed probable that this would also be the case in the sodium acetate method, and that a complete precipitation of the chrome might be effected by adding ferric chloride before boiling with sodium acetate. This conjecture has proved correct, and the author has thus succeeded in extending the sodium acetate method to chromiferous substances. About 5 atoms of iron are required for the precipitation of 1 atom of chrome on boiling with sodium acetate, and it is therefore needful to introduce the required quantity of ferric chloride into the solution without letting the excess become too great. The following is the best method of operating:—After dissolving the chromiferous ammonium sulphide precipitate in dilute hydrochloric acid and oxidising the solution with nitric acid, a small portion is tested for iron. In the absence of appreciable quantities of this metal the liquid is strongly diluted, the excess of acid removed by neutralisation, a little ferric chloride and sodium acetate are added, and a small specimen is boiled for a few minutes and filtered. If a sufficiency of iron was present or has been added the filtrate of this specimen is perfectly colourless, and does not turn yellow if warmed with hydrogen peroxide and caustic soda; a colour is produced by the formation of sodium chromate if any chrome compounds exist in the filtrate. (In presence of manganese compounds a second filtration must be performed to detect the colour). If chrome has been found in the filtrate, more ferric chloride is added to the main bulk until another small specimen shows the total precipitation of the chromium oxide. The whole quantity of liquid is then boiled for ten minutes and filtered. It is then certain that zinc and manganese remain in solution, whilst iron, aluminium, and chromium are quantitatively present in the precipitate.

In no case must the entire liquid mixed with sodium acetate be boiled until a sufficiency of ferric salt is present, since, as Reinitzer has observed and the author has confirmed, any chrome acetate, after boiling with ferric acetate, forms a so-called passive solution, from which neither chrome nor iron can be thrown down on a further addition of ferric chloride.

The precipitate is dried in the ordinary manner, fused with soda and saltpetre, and the alkaline chromate is extracted with water. Or the method proposed by Carnot (*Comptes Rendus*, cvii., p. 997) may be applied, which is, however, less advantageous.

In the simultaneous presence of chromium and phosphoric acid the sufficiency of the addition of ferric chloride must be ascertained not merely by the yellow precipitate given by soda-lye, but by the method indicated above (boiling with sodium acetate).

It is to be noted that if an equivalent quantity of a solution of aluminium was added in place of the iron, the chromium oxide was not completely precipitated. If a sufficiency of ferric chloride is present the chromim hydroxide is precipitated, even in presence of aluminium salts.

The hydrogen peroxide of commerce is sometimes completely useless for analytical purposes on account of such coarse impurities as barium chloride and salts of aluminium.—*Berichte d. Deutschen Chem. Gesellschaft* (vol. xxii., p. 2627).

MAGNESIUM BRONZE.

By H. N. WARREN, Research Analyst.

During the past week my attention having been drawn to the manufacture of magnesium bronze, I trust the following details may be observed with interest.

For the production of the various samples two ounces of metallic copper, contained in a graphite crucible, were raised to the melting-point by the aid of an injector-furnace, and upon its surface was projected half an ounce of magnesium metal; over this, melted borax was poured to prevent oxidation; the magnesium for a few moments burnt with intensity, the reaction quickly subsiding and proceeding tranquilly, emitting at intervals flashes of light characteristic of the metal. The crucible with its contents was now taken from the furnace, allowed to cool, and the metallic button extracted and examined as follows:—

The surface having been polished by the aid of fine sand, presented in appearance a highly zinciferous brass; on applying the hammer to the same, the ingot broke into various pieces, even under the influence of a slight stroke, and proved sufficiently brittle to be readily pulverised. Its solubility, oxidising properties, and fusing-point all closely resembled an ordinary brass. The analysis of the alloy showing 11 per cent magnesium; this was effected by dissolving the metal in nitric acid, precipitating the copper as oxide by means of soda, well washing the precipitate to free it from nitrates, and re-dissolving in hydrochloric acid, afterwards precipitating the whole of the copper by means of metallic magnesium. Washing the reduced copper thus obtained, and drying the same in an atmosphere of hydrogen; after cooling, weighing the metal, and calculating the difference to magnesium.

The remainder of the alloy was re-melted with the addition of various percentages of copper, and the former tests applied, the regulus becoming less brittle as the percentage of copper was increased, until an alloy containing 4 per cent magnesium was obtained, presenting in appearance a true bronze, and resembling the same as regards its physical properties, admitting of either being worked with the saw or readily turned. The experiments were further maintained until 1½ per cent of magnesium existed; this, although a small percentage, readily affected the copper, both by bleaching, and, to a certain extent, hardening the same. In short, the various alloys of copper and magnesium thus produced do not appear to excel, in general properties, the more common and, at the same time, more readily formed alloys of copper.

Everton Research Laboratory,
18, Albion Street, Everton, Liverpool.

THE INFLUENCE OF SILICON ON THE PROPERTIES OF STEEL.*

The Committee, having asked Mr. R. A. Hadfield to assist them in this investigation, beg leave to present the result of a series of experiments kindly undertaken by him.

Alloys of Iron and Silicon. By R. A. Hadfield.

The alloying of elements other than carbon with iron is a comparatively new field, and possesses special interest, not only to those concerned and engaged in the treatment of metals, but also to those who study the physical properties of substances. As the nature of alloys of carbon and iron is fairly well understood, it is hardly necessary to consider them here, and in order to narrow down the considerations dealt with in this paper to a practicable limit, attention will be confined solely to alloys or mixtures of which metallic iron and silicon form the principal constituents.

An investigation of the properties of manganese steel, *i.e.*, an alloy of iron and manganese, was placed before the Institution of Civil Engineers and Iron and Steel Institute by the author some twelve months ago, and its physical properties have been fairly well determined as compared with alloys of iron with other elements. This was the more practicable owing to the fact that the manufacture of "cast-iron" alloys of manganese—that is, ferro-manganese, has been for some time past in a very advanced state. In other words, by the cheap production of the alloys known as rich ferro-manganese—a material containing 80 per cent of ferro-manganese, 5 per cent to 7 per cent of carbon, and the rest iron, has enabled experiments to be readily carried out by further alloying such rich manganese products with pure iron.

Mr. Turner's paper, read before this Association at Bath last year, described experiments with steel containing from 0·10 per cent to 0·50 per cent silicon, and the details were fully given in the *Transactions*. The writer was asked by Mr. Turner and your Committee to investigate the effect of higher percentages of silicon.

The subject of alloys of iron and silicon has for some years occupied the writer's attention, but it is only lately that rich cast-iron alloys of silicon, *i.e.*, ferro-silicon, have been obtainable; and even now they cannot compare in richness of silicon with that of the manganese in ferro-manganese. The highest ferro-silicon yet made contains not more than about 18 per cent to 20 per cent of silicon. Fortunately, however, owing to the peculiar fact, noticed more fully further on, as to its lowness in carbon, this is much better fitted for experimental work as compared with, say, 20 per cent ferro-manganese. Such percentage of silicon, though, comparatively speaking, not so high, is sufficient to enable a suitable experimental material to be made, *i.e.*, a resultant material not containing too much carbon to interfere with an examination of the effect of the metalloid silicon upon the metal iron. Thus, while in the case of rich spiegel or ferro-manganese the carbon present amounts to some 5 per cent or 6 per cent, the 20 per cent ferro-silicon, on the contrary, contains comparatively little carbon—always under 1½ per cent, and often under ¾ per cent; so that by means of this cast-iron alloy, when further diluted or mixed with pure iron, the malleable material or steel produced practically contains but little carbon. The curious fact that ferro-silicon alloys as they rise in silicon diminish in carbon, was first noticed in some laboratory experiments eighteen years ago by Mr. Edward Riley; this will be again referred to further on. Whilst the scope of the experiments described in the present paper is in no way to deal with material other than malleable compounds of iron and silicon with small quantities of iron and manganese, it may be useful to give some general reference to previous experiments.

The only commercial employment of silicon with other metals is that of silicon bronzes. It is stated to act upon the copper in a similar manner to phosphorus. The qualities of such alloys are great strength and tenacity, high electrical conductivity, and resistance to corrosion. Wire made of this material is stated to have a conductivity of 80 per cent, and a tensile strength of about 36 tons per square inch.

Mr. Warren, in a recent number of the Chemical News, states that silicon, when in the nascent state, converts platinum into a brittle silicide; or, by heating graphitoidal silicon in contact with platinum to a full red heat, combination at once takes place, resulting in a brittle regulus containing as high as 10 per cent silicon, which is fusible at a red heat, and breaks with a crystalline fracture.

Silver and gold are reported as not presenting any great affinity towards silicon, but on heating a mixture of potassium silico-fluoride with either silver or gold in an amorphous condition to a high temperature, a well-fused regulus of silicide of the metal may be obtained. In the latter instance an alloy containing 5 per cent of silicon is almost as brittle as antimony. Silver, when alloyed with 10 per cent of silicon is stated to have a slightly red tint.

Rich cast-iron alloys of silicon are now usually described respectively as ferro-silicon and silicon-spiegel, the latter containing manganese in addition to silicon. Siliceous alloys of cast-iron were usually known as glazed pigs, owing to their peculiar glazed appearance when fractured. It is curious that this very material—burnt pig, as it was often called, and only then made accidentally—was formerly thrown on one side as useless, whereas now it is made purposely on a commercial scale and in large quantities—another of the many proofs of the advantage of bringing scientific knowledge to bear upon industrial metallurgy. Such ferro-silicon in itself

* Third Report of the Committee, consisting of Professors Tilden and W. Chandler Roberts-Austen and Mr. T. Turner (Secretary), appointed for the purpose of investigating the Influence of Silicon on the Properties of Steel. Read before the British Association, Section B, Newcastle Meeting.

alone is perfectly useless in the refinery or puddling furnace or for iron castings. The early samples of siliceous iron seldom contained more than from 4 per cent to 6 per cent of silicon; But Mr. Riley, of London, in 1872, was the first to point out that rich ferro-silicon was likely to play an important part in metallurgical industry. By means of laboratory experiments, he made in the crucible samples containing as high as 22 per cent of silicon. He also discovered that as silicon increased carbon decreased, until with 20 per cent of the former the latter was not present in quantities of more than ¾ per cent to 1 per cent, and the greater part of this small amount existed as graphite. Spiegeleisen and ferro-manganese are the richest carbon alloys that can be produced, and they contain about 6 per cent of carbon; ordinary cast-iron rarely exceeds more than about 4 per cent, and never more than about 4½ per cent. So strong, however, is the action of silicon in preventing carbonisation, even in the presence of a large excess of carbonaceous fuel, that in silicon-spiegel, an alloy of iron, manganese, silicon, and carbon, and notwithstanding the presence of a large amount of manganese, it—that is, the silicon—had still the upper hand, and prevents, as in the case of ferro-silicon, carbonisation taking place. A few typical analyses of ferro-silicon, silicon-spiegel, ferro-manganese, and spiegeleisen may be of interest here (see Table I.); for a fuller description, and for the methods of manufacture employed in their production, reference is given to Mr. Holgate's admirable paper on "The Composition of Ferro-Manganese and Ferro-Silicon made in the Blast Furnace." The writer is indebted to that paper for the analyses in question. Four of the samples quoted represent spiegel and ferro-manganese; and it is interesting to note that as the manganese rises there is a gradual increase of carbon up to as high as 7 per cent. A noteworthy fact is that if silicon, even in 50 per cent ferro-manganese, is allowed to reach 4 per cent the carbon is at once much reduced, in some cases to the low amount of about 2½ per cent. This action is still more intensified in the alloys known as silicon-spiegel or silicide of manganese, of which two analyses are given. From the latter it will be seen that, provided the silicon exceeds 10 per cent, the carbon is reduced to an exceedingly low point, and that although manganese may be present even in comparatively high percentages this is quite immaterial. This decrease of carbon takes place both in the combined and graphitic form, but principally in the former. A very valuable property of these spiegel alloys is the fact that they contain practically no sulphur, the much-dreaded enemy of the steel maker.

Table I.—*Analyses of Spiegel, Ferro-Manganese, Silicon-Spiegel, and Ferro-Silicon.*

	Analysis per cent.			
	Carbon.			
	Graphite.	Combined.	Silicon.	Manganese.
Analyses of spiegel and ferro-manganese, showing the gradual increase of carbon as the manganese increases.	—	4·27	0·110	8·11
	—	4·78	0·52	19·74
	—	5·63	0·42	41·82
	—	6·53	0·97	80·04
	—	7·20	0·14	80·04
Analyses of special manganese, showing that if the silicon becomes high the carbon diminishes very considerably.	—	3·56	4·90	23·90
	—	2·56	4·20	50·00
Analyses of silicon-spiegel or silicide of manganese.	0·33	1·85	10·74	19·64
	0·67	0·98	12·60	19 74
	0·90	0·30	15·94	24·36
Analyses of ferro-silicon.	2·35	0·05	8·77	2·42
	1·85	0·06	11·20	2·78
	1·20	0·23	14·00	1·95
	0·55	0·11	17·80	1·07

Remarks.—Sulphur and phosphorus practically absent, remainder being iron.

Note.—These Analyses are from the paper of Mr. Holgate, Assoc.R S.M. Darwen, on "The Manufacture of Ferro-Manganese and Ferro-Silicon in the Blast-Furnace."

It will therefore be seen that in the blast-furnace, somewhat strange to say, silicon cannot be reduced without carbon is also present; yet, when reduction of silicon occurs with the production of highly siliceous iron, carbon is practically absent in the resultant material. The late Dr. Percy, more than twenty years ago, referred to this in his "Metallurgy," and said that according to his experience no reduction can take place when silica and iron, without carbon, are heated together, even at the highest furnace temperature. Possibly this might now be accomplished in the powerful electric smelting furnaces, and it would be interesting to know whether alloys as rich in silicon as are the present valuable alloys of ferro-manganese rich in manganese could be produced. If so, without doubt, considerable employment could be found for them in metallurgical industry.

Alloys or compounds of iron, carbon, and silicon, non-malleable in their nature, and coming under the term "cast-iron," have been thoroughly investigated in this country by Mr. T. Turner, of Birmingham, the Secretary of our B.A. Committee, and the results placed before the Iron and Steel Institute, so that it is unnecessary to do more than touch upon this matter here. Great credit is due to this investigator for the lengthy and valuable researches he has made in this direction, as also to Mr. Keep, of Detroit, U.S.A., who has lately presented interesting papers on the same subject to the American Institute of Mining Engineers. Mr. Keep sums up so well the general results of all investigations up to date, that it may be well to briefly mention them, especially as some of the remarks apply to a great extent to the malleable compounds or alloys of iron or silicon now being described. Both Mr. Keep and Mr. Turner find that white carbonaceous cast-iron, which would invariably give porous and brittle castings, are made free from honeycombs, and possess much greater strength by the addition of comparatively small amounts of silicon: the latter result as to gain in strength is one which was considered contrary to previous experience. If further additions are made, say up to 2 per cent, the iron becomes grey, and at this point the maximum strength is obtained. If more silicon is added, although the iron becomes still more grey it also becomes weaker. By a still further addition a closer grain results, but it is even more brittle than in its white condition. Too much silicon also produces, as in the silicon steel now being described, lack of fluidity and greater shrinkage. Mr. Keep thinks that silicon in cast-iron is evidently, to some extent, combined with the iron and carbon; but whether it exists also in the form corresponding with graphitic carbon, mechanically mixed with the remaining mass, is a question still in dispute and unanswered. As now well known, the principal effect of silicon is to change the carbon from the combined to the graphitic state. One point particularly mentioned by Mr. Keep, and an important one, is that silicon irons have always had the reputation of imparting fluidity to other brands; and naturally this was at first supposed to be owing to the silicon added. It has now been found that this is not directly so, and that it is merely from the fact that the silicon present causes an increase in the quantity of graphite, and consequently a more fluid cast-iron. It is not, therefore, directly the cause except by its indirect action on the carbon.

In conclusion on this point, Mr. Snelus said, more than seventeen years ago, it is generally supposed that the absorption of much silicon tends to set free the carbon in the graphitic state. No statement more concisely expresses the influence of silicon on what is termed cast-

iron than that given some eight years ago by Mr. C. F. King, of Newport, U.S.A., in an able paper read before the American Institute of Mining Engineers on "The Chemical Action of the Bessemer Process." He said it is due to the presence of silicon in pig-iron that carbon is set free on cooling, and it is in proportion to the elimination of the silicon that the carbon remains chemically combined. Mr. King gives a diagram showing the rate of elimination of the metalloids in the process named, and it is a somewhat remarkable coincidence that the percentage point (1·8 per cent silicon), where the diminishing silicon curve cuts the combined carbon and graphitic curves, is exactly that which gave the maximum tensile strength in the material made by Mr. T. Turner, and later by Mr. Keep, in their numerous tests as to the effect of silicon upon cast-iron. The diagram referred to shows that by a diminution in the silicon highly graphitic pig-iron becomes rapidly mottled, and eventually white, although, practically, none or but little total carbon is oxidised, and this, as far as can be seen, solely by the fall of the silicon from 2·50 to 1·70 per cent. Whilst, therefore, Messrs. Turner and Keep show that white iron can be converted into mottled, and eventually grey, by means of additions of silicon, this diagram shows the converse, namely, that with silicon abstracted grey cast-iron becomes mottled and eventually white.

(To be continued).

SOME CONSIDERATIONS IN REGARD TO THE FORMATION OF COAL AND CARBONACEOUS MINERALS.

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(Concluded from p. 264).

Cannel used alone in gas-making, as in Edinburgh and Glasgow, gives a tar yielding less benzine and its homologues than that from bituminous coal, and these are mixed with a notable proportion of fatty hydrocarbons. From this tar olefins and paraffins boiling from 20° to 100° C. are obtainable, and of the liquid obtained at the boiling-point of benzine, only about two-thirds consist of that substance which crystallises out when the mixture is placed in ice and salt. On distilling cannel tar only about ten per cent of oils are obtained, which are lighter than water, about thirty-five per cent on the tar being heavier, and although the lower fractions contain notable quantities of fatty hydrocarbons, these gradually decrease until the heavy pitch-oil contains mere traces of paraffins. I speak here of the low heats used in gas-making thirty years since; with the high heats employed now-a-days the quantity of light hydrocarbons is much smaller, not above four to five per cent. On the other hand, cannel has been little used for low temperature work (except Leeswood cannel, which was what we would call here kerosene shale), although the amount of volatile hydrocarbons it contains ranges from forty to forty-five per cent, and even higher in Scotch cannels, where shales yielding thirteen per cent of oil are worked. Cannel oil in my experience is troublesome to purify, yielding much tar (polymerised acetylenes, &c.) to sulphuric acid.

Shale is very rarely used alone for making gas, but it is so used for the gas for the railway carriages on our Government railways. I tried to procure a sample of the tar, but found that unfortunately it could not be kept separate from the tar from bituminous coal, from which gas is also made. The mixed tar was just heavier than water, and particularly mobile for a tar. Subjected to distillation, the process being carried so far that the residue in the retort set to a rather hard pitch on cooling, it gave a distillate wholly lighter than water. This distillate treated by reagents gave the following percentages by bulk:—

8·5 per cent to concentrated sulphuric acid—basic bodies and polymerised acetylenes.
31·9 per cent sodium hydrate—phenols—and conjugate acid bodies formed by previous treatment with acid.
46·7 per cent to nitric acid—aromatic hydrocarbons and olefins.
12·7 per cent unattacked—paraffins.

99·8

As the shale used gives on low temperature-distillation a refined product containing paraffins to olefins in the ratio of 3 to 7, the 12·7 per cent above would give 29·6 per cent of olefins, which, added to 12·7, gives 42·3 per cent of fatty hydrocarbons, and subtracted from 46·7 gives 17·1 per cent of aromatic. If we consider that the amount of phenols extracted by soda from coal-tar is about 6 per cent, and this added at the same rate to the 17·1 per cent of aromatic hydrocarbon, would give 18·2 per cent of coal-tar hydrocarbons, and we would then have 18·2 coal hydrocarbons to 42·3 of fatty or shale hydrocarbons, which is in the ratio of 1 to 2·32. I am informed by Mr. Inspector Mitchell that the quantities of material used in the gas works are 9⅛ tons of Newcastle coal and 7⅜ tons shale per week, and as coal gives approximately 10 gallons of tar per ton, whilst shale averages about 27 gallons, this would give the following ratios:—

Coal to shale as 1 : 0·82
Coal-tar to shale-tar as 1 : 2·29

which shows a tolerably close approach to the ratio of hydrocarbons actually found. In this only the more stable hydrocarbons which have been taken into consideration; but, look at the matter how we may, there seems no doubt that the fatty hydrocarbons remain true to their type, and are much less readily converted into the higher carbon aromatics than is usually assumed under the conditions of high temperature-distillation as carried out on a large scale. This is further shown in the fact that although numbers of inventors have proposed processes, and have taken out patents for the conversion of the comparatively low value fatty hydrocarbons into the higher value aromatic ones by passing the vapours through heated tubes and otherwise, none of these have been commercially successful in consequence of the loss being great in the form of lower fatty hydrocarbons, and the yield of aromatic therefore small.

The C_6 formula of cellulose has been thought to connect it with the aromatic series, but all transformations convert it into hydrocarbons, alcohols, and acids of the fatty series. On the other hand, ligno-cellulose, as found in jute and other bast fibres with a higher percentage of carbon and a lower of oxygen, does yield aromatic compounds—as hippuric acid during its digestion by herbivora — and by its giving pyrocatechuic acid by chlorination, and subsequent treatment of the chlorinated product by fusion with potash. Ligno-cellulose, however, treated with nitric and sulphuric acid, yields no aromatic nitro-derivatives, so that the benzine nucleus must be absent. This seems to connect ligno-cellulose with these coals, which do not yield valuable aromatics during distillation, that is, cokeing, steam, and splint. I do not enter further into the consideration of those coals at present.

Suberose, cutose, or adipo-cellulose, the principal constituent of cork and the cuticular envelopes of plant tissues, differs widely from ordinary cellulose, and yields, by all treatments, substances belonging to the fatty series, and it seems probable that if transformed into mineral coal it would retain its fatty character.

Published analyses of these three celluloses show the following numbers:—

	Cellulose.	Ligno-cellulose.	Apido-cellulose.
Carbon	44·6	47·0	73·66
Hydrogen ..	6·3	6·0	11·37
Oxygen	49·7	47·0	14·97

I shall now refer to the three varieties of coal usually subjected to distillation for their products, and shall take first bituminous coal, used for gas-making and yielding valuable aromatic hydrocarbons as a by-product. The published analyses of coals are of little value for comparison for the purpose in hand, as these analyses have been made from average samples of different seams to determine their commercial value, and so do not take into account the fact that almost every coal is made up of a mixture of heterogeneous materials varying from nearly pure carbon to substances containing large percentages of hydrogen and oxygen. Even in the different bands, into which coal seams are divided by partings, the average of each band may differ very considerably from the average of the whole. Thus in the six bands of a coal seam which I recently examined, the ratio of volatile hydrocarbon to fixed carbon was in each band.

No. 1..	1 : 1·977
„ 2..	1 : 2·750
„ 3..	1 : 2·349
„ 4..	1 : 3·075
„ 5..	1 : 2·260
„ 6..	1 : 1·122

It appears doubtful whether much information could be got from making ultimate analyses of the separated constituents of any coal (except in the case of the substance No. 1 below, which I shall examine further), and I have confined myself to determining the hydrocarbons driven off at a cherry-red heat from different materials in the same block of coal.

In some Newcastle coal, colliery unknown, a piece was separated into jet-black bituminous matter, which broke easily into more or less cubical fragments, and a dense hard coal with a rather pale lustre. Subjected to heat the bituminous portion fused together, forming a swollen bright coke, whilst the other did not fuse, but shrank slightly, and gave a coke of the same shape as the original, or nearly so, and silvery. The ratio of volatile matters to fixed carbon was—

	Volatile.		Fixed carbon.	Ash.
In No. 1 ..	1	:	2·012	0·52 per cent.
„ 2 ..	1	:	3·455	9·81 „

The ash in No. 1 was composed almost entirely of ferric oxide; that of No. 2 was greyish.

A piece of Stockton coal, which is considered one of the best of our Newcastle coals for gas-making, similar in appearance to the first, gave--

	Volatile.		Fixed carbon.	Ash.
No. 3 ..	1	:	1·870	1·12 per cent.

In this case also the ash was almost entirely composed of oxide of iron. This coal is bituminous to such an extent that I could not get enough non-bituminous to examine by itself.

The coals of our Western districts are much less bituminous than in the Northern, and the bituminous matter is in very thin layers. From No. 4, the bright black portion of a piece of Lithgow Valley coal, and from No. 5, the contiguous dull portion, I got—

	Volatile.		Fixed carbon.	Ash.
No. 4 ..	1	:	1·889	1·07 per cent.
„ 5 ..	1	:	2·248	5·63 „

No. 4 swelled up and united into a single mass, but did not so entirely lose its original outline as in the case of No. 1, and it was lustrous black, not silvery. The ash consisted chiefly of alumina with a little oxide of iron and some traces of silica.

In No. 5 the coke was shrunk, and of the same shape as the coal. There were some bright black thread-like bands in No. 5 which it was impossible to remove, and these probably raised the percentage of volatile matter. I could not avoid this, as I wished to have the portions of coal immediately contiguous.

Those results seem to indicate that the bituminous part arises from altered resin, from the low ratio of fixed carbon, and the low percentage of ash; in the case of those from Newcastle, oxide of iron, which could be introduced by infiltration, as could also be the case with the alumina in the Lithgow Valley, as the water of the overlying Hawkesbury Sandstone generally contains sulphate of alumina in solution.

In connection with a coal from Mittagong, the analysis of which was published in the "Annual Report of the Department of Mines," in 1878, I made the following remark, which has been reproduced in Professor Liversidge's "Minerals of New South Wales":—

"The bright lines of fracture were marked by numerous lens-shaped cavities 00·5 to 0·10 inch in greater diameter, generally filled with a brownish pulverulent carbonaceous matter. These were apparently the impressions and remains of seeds, and they showed traces of a dense cortical layer. The bituminous matter on heating glowed, emitted a smoky odour, and burned away completely."

These seeds were quite absent except in the bright layers. Now if the seeds fell and were enclosed in resin, germination would be prevented and they would be preserved, whilst if they fell in decaying vegetable matter all traces of them would be lost.

I conclude, therefore, that the bituminous coals yielding low and valuable hydrocarbons on distillation are originally derived from aromatic resin-bearing plants, the resinous ligno-cellulose of which contributed to the result; whilst the cambium or more cellulosic portions were mostly lost by decay, a little being converted into mineral charcoal. We can see the preservation of resin in retinite and also in the more recent Kauri and grass-tree gums, where the cellulose has often disappeared.

Cannel.—I have no analysis of my own of this mineral, but give below the ratio of volatile matter and fixed carbons from two analyses given in Percy's "Fuel" and one from "Watts's Dictionary." In nearly all books analyses of true cannels are mixed up with those of torbanite or kerosene shale from Bathgate and elsewhere.

The Lesmahagow is a true typical cannel from the middle ward of Lanarkshire, and there called candle coal (pronounced caun'l), where it was first used to give light in the farmhouse kitchens, a lump being put on the red fire in the evening.

	Volatile.		Fixed carbon.	Ash.
Lesmahagow ..	1	:	1·495	6·03 per cent.
Wigan	1	:	1·304	2·40 „
Mold	1	:	1·188	—

Cannel differs from bituminous coal in being of a nearly uniform texture, in which it resembles torbanite, but differs from the latter in every other way. From the character of the hydrocarbons it yields on distillation, it seems probably derived from adipo-cellulose, and ligno-cellulose, the former having considerable development in plants, which, from the comparative uniformity of the mineral, were probably of small size.

Torbanite or Kerosene Shale.—In the coals and cannels the volatile hydrocarbons are always less than the fixed carbon, whilst in the shales this ratio is always reversed and that irrespective of the amount of ash present. The following are five recent determinations of mine, the carbon being the smaller is taken as No. 1, not the volatile matter as in the coals:—

	Carbon.	Volatile hydrocarbon.	Ash.
No. 1. Joadja Creek.. ..	1 :	16·908	6·17
„ 2. Source unknown ..	1 :	12·500	6·20
„ 3. Murrurundi	1 :	8·625	21·32
„ 4. „	1 :	6·041	40·88
„ 5. United States ..	1 :	2·561	7·95

Nos. 1 and 2 were beautiful fine-grained shales, with a velvety lustre and pale streak.

No. 3, fine-grained brownish, scarcely velvety.

No. 4, coarse-grained brownish, dull.

No. 5, black, dull—streak dark brown, almost black.

It will be observed that the ratios in these shales differ widely, and also that the percentage of ash has a great range, but the value of the shale for distillation, either for oil or gas, appears to depend more on the ratio of hydrocarbons to fixed carbon than upon the quantity of ash. Thus, No. 3 is a shale much superior, whilst No. 4 is very little inferior to No. 5, although it contains more than five times as much ash. I refer to the quantity of gas or oil yielded. If distilled for oil, No. 5 would yield a very bad quality, the distillate containing much tar. This shale approaches in appearance the outlying portions of the better shales where they have been pinched under heavy cover.

Looking at the ultimate composition of shale in conjunction with the yield of fatty hydrocarbons, I was at first inclined to consider it as a product of adipo-cellulose. The following are analyses—first, of torbanite from Bathgate given in "Watts's Dictionary"; second, of shale from Hartley, by Professor Liversidge, which I have calculated free from ash, and for comparison I repeat that of adipo-celluloses in the third column.

	I.	II.	III.
Carbon	79·6	79·67	73·66
Hydrogen..	11·2	12·92	11·37
Oxygen, nitrogen, and sulphur* ..	9·1	7·41	14·97
	99·9	100·00	100·00

I subjected some carefully selected cork in thin shavings as the nearest substitute for adipo-cellulose to a rapid red heat and also pure cellulose, and obtained the following ratios:—

	Fixed carbon.	Volatile matter.
Cork..	1 :	5·245
Cellulose.. ..	1 :	7·916

As under no conceivable conditions could the ratio of volatile matter be increased during the conversion into mineral, the similarity in composition goes for nothing.

It has been suggested by someone that the shales are the products of resinous spores of some plant. From the persistent fatty products of distillation I think resin must be abandoned as resins pass more to aromatics. It appears to me more probable that shale comes from some oil or wax producing plant, more likely the latter, in view of the considerable yield of solid paraffin.

The shale at Joadja Creek is very uniform in texture: there is here and there a star-like speck of so-called jet, and rarely a ribbon-like piece of the same running through a block, perhaps an inch or so wide and barely an eighth of an inch thick. As there is bituminous coal above, these may represent resinous roots, but I could not get any for examination in time for this paper. At Joadja there is a ligno-cellulose coal below, a wax shale in the middle, and a resinous ligno-cellulose coal above.

Several other points have occurred to me since I promised this paper for the meeting of the Association, but pressure of other work has prevented me going into them.

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* The sulphur and nitrogen are very small in these shales. The only difference is an increase of carbon and a decrease of oxygen in the shales.

Addendum, September 29.—Since writing the above paper I have found in my notes an analysis of the best Joadja Creek shale, for which I had before looked in vain. In the first column is given the analysis; in the second the carbon, hydrogen, and oxygen only, eliminating the other ingredients as extraneous; in the third the numbers for the formula $C_{34}H_{64}O_2$, that is, a paraffin with 4H replaced by 2O (calculated).

	I.	II.	III.
Carbon	75·32	81·10	C_{34} 80·95
Hydrogen	12·05	12·97	H_{64} 12·69
Oxygen	5·49	5·93	O_2 6·33
Nitrogen	0·28	—	—
Sulphur	0·31	—	—
Ash	6·55	—	—
	100·00	100·00	

Pyrites was observed in the shale and was probably the source of the sulphur.

I do not attach much importance to the formula obtained, as the organic matter of shale is not a pure substance, though I think an approach thereto. For comparison there are given below some analyses of waxes. First, myricin or myricyl-palmatate (calculated); second, ceroxylin or palm wax, the average of three analysis by Boussingault, Lewy, and Teschemacher ("Watts's Dictionary," i., 837); third, carnabau wax by Lewy ("Watts's Dictionary," i., 805); fourth, occuba wax by Lewy ("Watts's Dictionary," iv., 173); and fifth, tristearin (calculated).

	I.	II.	II.	IV.	V.
Carbon	79·31	80·74	80·30	74·0	76·8
Hydrogen ..	13·22	13·26	13·00	11·3	12·3
Oxygen.. ..	7·47	7·00	6·70	14·7	10·9

Occuba wax (No. 4), the product of a plant growing in marshy places in South America, is not a true wax, but a mixture of solid fats.

It seems evident that the organic matter of shale, if produced, as I think probable, from a vegetable secretion, must have been so produced by the elimination of hydrogen and oxygen in the form of water, with probably elimination of hydrogen also by atmospheric oxygen, and could not arise from either of the last two, which contain less hydrogen, and still less could it arise from fats of lower molecular weight than tristearin, whilst it is possible from the waxes. This is more clearly seen if in Nos. 4 and 5 the hydrogen and oxygen are calculated for a quantity of carbon equal to that in the shale, thus:—

	IV.	V.
Carbon (as in shale)	81·10	81·10
Hydrogen	12·39	12·98
Oxygen..	16·11	11·52

The first shows less hydrogen than the shale, the last an equal quantity, but in both there is a large percentage of oxygen to remove hydrogen, which is not the case with the waxes, in which indeed the oxygen is rather deficient, which deficiency could be supplied by atmospheric oxygen.

The objection to derivation from fats apply with even greater force to the derivation from amber (succinite) and similar mineral resins, probably little altered in constitution, a connection claimed by Dana in Bathvillite ("Mineralogy," p. 742), as amber contains much less hydrogen than Bathvillite or shale.

The organic matter of the shale of this country is evidently a very stable body. It is almost absolutely insoluble in naphtha, carbon bisulphide, and similar menstrua. It is scarcely acted on by exposure to the weather, as for years subjected to fierce sun in summer, frost in winter, and rain at all times, it only becomes slightly brown on the immediate surface. Long continued

boiling with caustic alkali dissolves from the powder, only a trace of humus-like matter and fusion with caustic potash for two hours gives a similar result, whilst amber is soluble in alkalies. The bituminous matter of coal is insoluble in solution of caustic potash, but fusion with potassium hydrate renders it largely soluble in water. In this respect it is different from the "jet" mentioned above, which is insoluble in such menstrua as carbon bisulphide, &c., in caustic potash solution, and long fusion with caustic potash gives no more soluble matter than is obtained from the shale itself,

This "jet" subjected quickly to a cherry-red heat gives—

Volatile matter	41·12
Carbon*..	55·80
Ash..	3·08

The ash was reddish-coloured from the presence of oxide of iron. The immediately adjacent shale gave 9·16 per cent of white ash, whilst the volatile matter was 83·62 per cent and the fixed carbon 7·21, indicating a radically different original constitution from the jet, although in some respects that was different from the bituminous matter of coal.—*Proceedings of Australasian Association for the Advancement of Science*, Sydney, 1888.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, November 21st, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. James Munro Taylor Anderson, Edgar House, Combs, Suffolk; George Frederick Brindley, Aluminium Company, Oldbury, near Birmingham; Philip Howard Davis, 106, Talcott Road, S.W.; Alexander Charles Farquharson, 13, Stonebyres Terrace, Partick, Glasgow; P. J. Hartog, 6, Greville Road, London, N.W.; Robert Law, 70, Maxwell Road, Pollokshields, Glasgow; Hugh Marshall, 1, Lorne Terrace, Edinburgh; Francis Herbert Mason, Outalpa, Harlesden, N.W.; Edgar Philip Penman, B.Sc., 32, Oakington Road, Elgin Avenue, W.; Edward Russell, 75, Kelvin Road, Highbury Park, N.; Henry Heron Smith, Wilton House, Vicarage Park, Plumstead, S.E.; John Wade, 129, High Road, Lee, S.E.

The following papers were read:—

99. "*The Law of the Freezing-points of Solutions.*" By S. U. Pickering.

Although the influence which a substance exerts in lowering the freezing point of a solvent, when used with caution, may give valuable evidence as to its molecular weight in the quasi-gaseous condition, it is impossible to accept Raoult's statement of the observed facts as a general law of freezing-points. The so-called constant exhibits a variation of some 20 or 30 per cent in the case of different substances (not counting those cases where the values are admittedly abnormal), and may also vary to the same, or to a greater, extent, when different proportions of the same substance and solvent are taken, even when we confine our attention to cases where the proportion is that of not more than 1 mol. to 100 mols. of the solvent. Still less can we, on the strength of the supposed constancy of the value, draw any conclusion from it respecting the nature of solutions.

The author believes that he has found the law which regulates the freezing-point of a solution of any strength. He attributes the lowering produced by the dissolved substance to three distinct causes, which he classifies as (1) mechanical, (2) physical, and (3) chemical.

In the first place, he points out that if a weak solution (taking water as a concrete instance of a solvent) consists, as he maintains it does, of a hydrate, the water which crystallises out on cooling is derived from the hydrate itself; which is thermally possible, since the heat of solidification of the water is far in excess of the heat of formation of the hydrate. Hence the whole hydrate does not act as the "foreign molecule," but only that part of it which is not water, *e.g.*, H_2SO_4; and hence, also, the molecular weight obtained by Raoult's method is that of the H_2SO_4, and not that of the hydrate. But, although the decomposition of a complex hydrate into the next lower one and solid water is an exothermic change, such would not be the case with all the lower hydrates, and, in fact, the limit of possible decomposition is fixed very clearly at the hydrate containing $5{\cdot}5H_2O$. In the same way, the limits of the two branches of each of the curves representing the crystallisation of $H_2SO_4{\cdot}4H_2O$ and $H_2SO_4{\cdot}H_2O$, and that of the one branch of the H_2SO_4 curve, can be established from thermo-chemical considerations, and all these limits agree very well with the nature of the curves obtained experimentally.

1. *Mechanical Lowering.*—Considering the foreign molecules to be uniformly distributed throughout the solvent, and considering, also, for the sake of simplicity, that the molecules are stationary, the author argues that the solvent molecules will be entirely isolated from each other, and, therefore, will be prevented from combining to form the aggregates of which a solid is constituted, when there are 300 foreign molecules to every 100 molecules of the solvent. This value obtains only if we consider the molecules on a superficies, but the author argues on experimental as well as general grounds that crystallisation is entirely a surface action. The temperature below which a liquid will not solidify is −160°, according to Person (see *Trans.*, 1889, 32): hence 300 foreign molecules to the 100 will lower the freezing-point of water 160°, and one molecule will lower it by—

$$(160 \div 300 =)\ 0{\cdot}53°,$$

a constant closely approximating to that (0·63°) found by Raoult for various solvents freezing at about the same temperature as water. In the case of water, Raoult's work shows that the active molecule is not H_2O but $3H_2O$; the mechanical constant will, therefore, be $(0{\cdot}57 \times 3 =)\ 1{\cdot}6°$.

2. *Physical Lowering.*—If water be superfused to $t°$ below its normal freezing-point, and, then be made to crystallise, the heat evolved in its solidification diminishes regularly with the value for $t°$ from 1430 cal. per H_2O at 0° to *nil* at −160°; if $t°$ be −79°, or any lower temperature, the whole of the water will solidify, whereas for smaller values of t, the amount solidifying is given by—

$$\frac{t}{79},$$

and the heat evolved in this partial solidification will always be exactly sufficient to raise the resulting mixture of ice and water from $t°$ to 0°. If, however, we take a hydrate, say, $H_2SO_4 13H_2O$, the freezing-point (water crystallising out) of which is −34°, the total water available for crystallisation is only $7{\cdot}5H_2O$, for no amount of cold would suffice to decompose the residual hydrate $H_2SO_4 5{\cdot}5H_2O$; the amount of water which would crystallise would, therefore, be $\frac{34}{79}$ of $7{\cdot}5H_2O$, or $3{\cdot}2124H_2O$, and the heat evolved in its crystallisation is easily calculated, being 3615 cal. After the crystallisation a mixture of $3{\cdot}2124H_2O$ as ice, $(7{\cdot}5-3{\cdot}2124)H_2O$ as water and $H_2SO_4 5{\cdot}5H_2O$ would remain, the total heat capacity of which is 223·5, and this mixture would be raised 16·17° by the 3615 cal. evolved, instead of 34° as would have been the case had there been nothing but the water present. The freezing-point, therefore, will have been lowered $(34°-16{\cdot}17°=)\ 17{\cdot}83°$ from this "physical" cause.

3. *Chemical Lowering.*—A definite hydrate such as

* The carbon was left as a highly intumesced bright coke.

$H_2SO_4 13H_2O$ can only give up its water by decomposing into the next lower hydrate, $H_2SO_4 9H_2O$, in the instance taken: the heat absorbed in this change is given by the heat of dissolution curve (863 cal.), and will lower the temperature of a mixture with a heat capacity of 223·5 cal. by 3·5°.

The sum of these three lowerings gives −33·64° as the freezing-point, whereas −34·0° is the value obtained. The former is more strictly a calculated verification of the observed value than a calculated value; but it is in calculating the physical lowering only that the observed value is taken to start with, and the author finds that if a wrong value be taken for the freezing-point the "calculated" value does not agree with it, and that by a series of approximations we might ultimately obtain the true value starting with any temperature in the first instance. The following instances may be quoted:—

Hydrate.	Per cent H_2SO_4.	F. p. found.	F. p. calculated.
H_2SO_4,130H_2O	4·02	−1·59	−1·39
,, 60 ,, ...	8·59	−3·80	−3·44
,, 24 ,, ...	18·49	−11·83	−11·52
,, 13 ,, ...	29·53	−34·00	−33·64
,, 9 , ...	37·70	−72·63	−72·77

After the hydrate with $13H_2O$, the active water-molecule becomes simplified, attaining the formula H_2O before the hydrate with $9H_2O$ is reached. A similar simplification has been observed at about the same molecular composition in the case of mixtures of alcohol and water. Instead of calculating the freezing point, we may take the observed freezing-point and calculate the heat evolved in the chemical action, and, hence, the composition of the next lower hydrate formed in the reaction. The values given by the last three of the above-mentioned freezing-points are—

	Found. Per cent.	Calculated. Per cent.
Position of next hydrate	29·5	31·1
,, ,, ...	37·7	38·5
,, ,, ...	49·8	49·5

In the other two cases the chemical lowering is so small in comparison with the errors inherent in the calculations, that the calculated position of the next hydrate is valueless.

If no definite hydrates existed in solution, the chemical lowering would be absent; its absence would always increase the discrepancy between the observed and calculated values, and in the last three cases would destroy all semblance of agreement, the differences amounting to from 1·6° to 10·3°.

In the case of very weak solutions (0·36 and 0·37 per cent), the actual error between the observed and calculated values is less than 0·01°, but this is a relatively large quantity, and is probably due to errors in the experimental method adopted. A very striking confirmation of the composition of the hydrates at these points may, however, be obtained by comparing the figures representing the found and calculated values. Very definite proof is thus obtained that the author was wrong in supposing the existence of a hydrate with $510H_2O$ (1·0 per cent), but right as to the others.

The correctness of the calculated values affords proof not only of the position of the next hydrate, but also of their being a hydrate of the composition of the solution at which the freezing-point is taken. Points intermediate between definite hydrates may be correctly calculated on the supposition that the liquid consists of a mixture of next higher and next lower hydrate; whereas, if the calculation be based on the wrong supposition that the liquid consists of one definite hydrate, wrong values are obtained; thus:—

$H_2SO_4 16H_2O$ = 25·4 p.c.: the f. p. found was −23·0°; that calculated for a mixture of $H_2SO_4 24H_2O$ and $H_2SO_4 13H_2O$ is −22·36°; that calculated for a definite hydrate is −20·75°.

Very strong evidence of the existence of certain definite hydrates may be deduced from the limit assigned on thermo-chemical grounds ($H_2SO_4 5·5H_2O$) to the decomposition of the hydrates. Thus, taking the f. p. of the solution, $H_2SO_4 13H_2O$, we get −34° as the found value, and −33·64 as the value calculated with the above-mentioned limit; whereas, if the limit be taken to be the next hydrate above or below that with $5·5H_2O$, namely, those with 9 and $4H_2O$, we get −41·51 and −30·18 as the calculated values respectively; and, more important still, if we take that limit which would hold good on the physical theory of there being no definite hydrates in solution, which limit would be at about $H_2SO_4 7H_2O$, we get −37·11° instead of −34° as the calculated value.

The results obtained in calculating the lowering of the freezing-point of sulphuric acid by the addition of water, do not, from several causes, agree so well with the observed values as in the case of the water curve; but the differences are not great, and, though they prevent the correct calculation of the composition of the hydrates present, they are not sufficient to prevent our drawing from them further important confirmation of the general truth of the author's theory, and of concluding that the active molecules are, in this case, H_2SO_4 and H_2O respectively. The results mentioned are the following:—

	Per cent.	F. p. found.	F. p. calculated.
$36H_2SO_4H_2O$ ..	92·49	−3·05°	−1·89°
12 ,, ..	98·49	−8·85	−7·38
6 ,, ..	97·03	−18·60	−16·97
3 ,, ..	94·23	−41·60	−38·61

These numbers representing degrees below the f. p. of the pure acid (10·35° C.).

In the case of the crystallisation of the monohydrate, the active molecule of sulphuric acid appears to be $12H_2SO_4$ throughout; while on the other branch of the curve where the f. p. is lowered by the addition of water, the "mechanical lowering" appears to be absent. This is probably due to the active molecule of water being very complex; if it were 12 times as big as it is when *it* is the crystallising substance (*i.e.*, the same proportion which obtains in the case of the sulphuric acid molecules), it would be $36H_2O$, and the lowering thereby produced would be practically negligible. The magnitude of the active molecules of the "foreign substance" in this case is probably due to the fact that the crystallising substance actually contains some of each of them, and therefore exerts less influence on them than would otherwise be the case. The fact that we have to determine the magnitude of the mechanical constant in the first instance from the curve does not detract much from the value of the deductions as to the calculated values; for one point is sufficient to give us the value of the constant, and we can then apply it in an indefinite number of other points. The instances given are—

Hydrate.	Per cent.	F. p. found.	F. p. calculated.	Next hydrate. Found. Per cent.	Next hydrate. Calculated. Per cent.
$H_2SO_4H_2O$,$\frac{1}{6}H_2SO_4$	86·40	−2·2	−2·36	89·10	88·46
,, $\frac{1}{2}$,, ...	89·10	−9·8	−10·14	94·23	93·65
,, 2 ,, ...	94·23	(−60·7)	−63·19	—	—
,, $\frac{1}{6}H_2O$	82·36	−2·10	−2·13	78·41	78·45
,, $\frac{1}{2}$,, ...	78·41	−15·41	−15·05	73·14	72·78

Of the 20 hydrates which the author has already announced as existing in the case of sulphuric acid, one has been definitely disproved by the present calculations; in the case of three others the evidence is insufficient to be termed proof; while proof of the most definite description is obtained in the case of the remaining. The hydrate $H_2SO_44H_2O$ is included, since the mere existence of the curve representing its crystallisation is ample proof of its existence, though there are no data existing in this case at present on which to found any calculations of the freezing-points.

Discussion.

Professor Ramsay said that it was impossible without careful study to offer any valuable criticism on so comprehensive a paper, opening up such new points of view. He drew attention to the fact that the supporters of Van't Hoff's theory of the existence of a substance dissolved in a liquid in a molecular state comparable with that of a gas by no means shut their eyes to the possibility, and in many cases the probability, of the existence of complex molecules, either of the solvent itself, or of compounds of the solvents with the dissolved substance. He also questioned the correctness of Person's data, on which it was assumed that the "solid-liquid critical point" was $-160°$, inasmuch as it is founded on insufficient data regarding the specific heats of solids and liquids at low temperatures. With reference to the sudden change in the molecular complexity of the water-molecule, assumed by Mr. Pickering to occur between the hydrate with $13H_2O$ and that with $9H_2O$, he suggested that a gradual disruption of the complex water-molecule would be more likely, and stated that from experiments of his own it appeared more probable that the water-molecule consists of $4H_2O$. The existence of complex molecules of sulphuric acid he regarded as supported by the fact of their being double sulphates of such formulæ as $NaH_7(SO_4)_4$.

Mr. Pickering, in reply, said that it was quite true that Person's "absolute zero" of $-160°$ was more or less hypothetical. But it was founded on considerations precisely analogous to those on which the "absolute zero" for gases, $-273°$, was founded; and, just as the latter, though hypothetical also, yields correct results in all cases where true gases are concerned, so the former yields correct results in the case of liquids. He pointed out that the change of the acting water-molecule from $3H_2O$ to H_2O was not sudden, but was spread over a range 8 per cent in the strength of the solutions. There were no signs of the change beginning before the solutions attained the composition $H_2SO_413H_2O$. Finally, although, according to Raoult's work, the active molecule of water in this and in the majority of cases appeared to be $3H_2O$, there were other instances in which it attained the magnitude $4H_2O$.

100. "*The Constituents of Flax.*" By C. F. Cross and E. J. Bevan.

The authors describe the results of their examination of the cuticular constituents of the fibre, the only investigation of which hitherto published is that of F. Hodges (*Proc. R. Irish Acad.*, 1881, iii., 460).

On exhaustion with boiling alcohol, the fibre loses 3—4 per cent of its weight; as the solution cools it deposits a greenish white resin, which on hydrolysis with alcoholic soda yields a wax alcohol, identified as ceryl-alcohol. In addition to the alcohol an oily ketone-like substance was obtained. The residue appeared to be unresolved: on submitting it to drastic treatment with alkalies, two fatty acids were obtained, one of which, from its equivalent and melting-point, appears to be a cerotic acid. A considerable residue of unresolved products remained.

The green filtrate from the resin-wax yielded on distillation a green oily residue. From this a further quantity (10 per cent) of ceryl alcohol was isolated, and a much larger proportion of the oily ketone (15 per cent); the residue being a complex of ill-defined, inert compounds, yielding "ketones" on hydrolysis. These "ketones" have the characteristic odour of raw flax and flax goods, and from their property of emulsifying with water, no doubt exercise an important influence on the wet processes of fine spinning of flax.

The pectic group of constituents associated with the cellulose in the fibre proper was found to yield mucic acid on oxidation with nitric acid ($d = 1{\cdot}15$).

The isolation of a pure cellulose from flax is a difficult operation. The presence of unremoved cuticular constituents accounts for the statements of Godeffroy, that flax cellulose reduces silver nitrate when boiled with a neutral solution of the salt, pure flax cellulose resembling cotton cellulose in resisting the action of this agent. Flax cellulose oxidised with permanganate in alkaline solution yields, in addition to oxy-cellulose and oxalic acid, acid bodies, from which furfurol is obtained by acid hydrolysis.

101. "*Acetylcarbinol* (*Acetol*), $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$." (Preliminary notice). By W. H. Perkin, Jun., and J. Bishop Tingle, Ph.D.

This important substance, the first member of the series of ketone alcohols, has never been isolated, although its dilute aqueous solution has repeatedly been obtained. The authors have succeeded in preparing it in an anhydrous condition by the following method:—25 grms. of monochloracetone is slowly added from a dropping funnel to 200 c.c. of water containing an excess of freshly precipitated barium carbonate in suspension, the whole being vigorously boiled during the operation. As soon as the monochloracetone has dissolved, and the evolution of carbon dioxide has practically ceased, the liquid is filtered, and the resulting almost colourless solution is distilled. The distillate is now treated with chloracetone and barium carbonate and again distilled, the operation being repeated until 150 grms. of chloracetone have been treated. The resulting moderately concentrated solution of acetylcarbinol is saturated with potassium carbonate, and extracted at least 50 times with pure ether. The ethereal solution is thoroughly dried by means of ignited potassium carbonate, and is then slowly evaporated; a colourless oil remains, the greater part of which passed over on distillation between 140° and 150°, On refractionating, a considerable quantity was obtained boiling at 145—150°, which gave on analysis numbers agreeing with the formula $CH_3{\cdot}CO{\cdot}CH_2{\cdot}OH$, viz., $C = 48{\cdot}73$ and $H = 8{\cdot}33$, instead of $C = 48{\cdot}65$ and $H = 8{\cdot}11$.

Two vapour-density determinations by Hofmann's method in xylene-vapour gave $d = 35$ and 34, instead of 37.

Acetylcarbinol is a colourless oil, possessing a faint and peculiar odour, and a sweet but burning taste. It is miscible with water, and very readily reduces Fehling's solution in the cold.

When heated with excess of phenylhydrazine, it is converted into its osazone,—

$$\begin{matrix} CH_3{\cdot}C{:}N_2HC_6H_5 \\ | \\ CH{:}NH_2C_6H_5 \end{matrix},$$

which melts at 145°. This substance has already been prepared by Laubmann (*Annalen*, ccxlii., p. 244), and is identical with the compound obtained by Pechmann (*Ber.*, xx., 2543) from methylglyoxal and nitrosoacetone.

NOTICES OF BOOKS.

The Photographic Quarterly. Edited by C. W. Hastings. No. 1, October, 1889. London: Hazell, Watson, and Viney.

This new publication is full of good matter, and must be said to make an excellent beginning. Mr. C. H. Bothamley, F.C.S., contributes a sound paper on the chemistry of photography. In impressing upon the photographer the importance of an acquaintance with chemistry, the writer says:—"If his previous training

has been of a purely literary character, his want of familiarity with the scientific method will increase the difficulty." Here the truth is admitted, as Prof. Galloway insists that a purely literary training positively incapacitates the mind for the study of science. Whilst fully recognising that there is only one chemistry, he urges that "the same fundamental principles may be demonstrated and illustrated by very different sets of facts." He regrets that no elementary chemical text-book especially designed for the photographer has yet been written. In the same connection he remarks most truly that "adaptation to the antique syllabuses of examining boards has fossilised along a certain groove opinion as to what facts ought to be included in an elementary text-book on chemistry; and the resemblance between the very numerous chemical text-books now in existence is very like the resemblance between an equal number of pods of peas." Mr. Bothamley speaks almost as feelingly as if he had had to review a few dozen of such manuals.

In a paper on the "Influence of Photography on Art," Mr. A. M. Rossi looks forward into the dim future, when "another genius higher even than Daguerre will add colour to the photograph with the same truthfulness and vividness of nature."

The paper on "Photomicrography" is perhaps the most important of all. We perceive only one error. The writer, Mr. J. Hall-Edwards, L.R.C.P., says:—"When we remember that the number of species of plants and insects at present known has been estimated at 100,000." This is sadly below the mark. In all probability the number of one order of insects alone, the *Coleoptera*, does not fall far short of 100,000.

Mr. W. Jerome Harrison, F.G.S., contributes an interesting paper on the question, Was Photography discovered a Century ago?

Six candidates are mentioned: Matthew Bolton and F. Eginton, of Soho, about 1777; Thomas Wedgwood, of Etruria, and Humphry Davy, between 1794 and 1802; Lord Brougham in 1795; and Prof. Charles, of Paris, about 1780.

Lord Brougham's claim rests on an unpublishd part of a paper and on an experiment suggested, but not actually tried, and which, if tried, would have failed. Prof. Charles's candidature was rejected by Arago as not resting upon documentary evidence. The drawings produced "by mechanical means" at Soho were specimens of a method of engraving on copper, probably "*aquatint*." The part played by Wedgwood and Davy was much more important, and is reserved for discussion in the January issue, to which we look forward with much interest.

A Text-Book of Organic Chemistry. By A. Bernthsen, Ph.D., Director of the Scientific Department in the Chief Laboratory of the Baden Aniline and Soda Manufactory; formerly Professor of Chemistry in the University of Heidelberg. Translated by G. M'Gowan, Ph.D., Demonstrator in Chemistry, University College of North Wales, Bangor. London: Blackie and Son.

The author of this work has aimed at producing a small text-book, which, while not exceeding some thirty sheets in size, and of which the descriptive portion was condensed as much as possible, should yet be of a strictly scientific character; a book which, beginning with homologous series, should lay especial emphasis upon summarising the characteristics of each class of compounds, and, wherever possible, upon the inductive development of the theoretical relations existing between them.

In carrying out this idea Dr. Bernthsen has added another to the fairly numerous army of chemical text-books already in existence; a book in which it might be hard to detect any error, but the *raison d'être* of which is not beyond question.

We are glad to find that Dr. M'Gowan has not deemed it necessary to modify the book in accordance with the demands, open or implied, of any syllabus or examining body.

A few expressions occur which can scarcely be considered as good English. Thus, we are particularly sorry to see magenta spoken of as "fuchsin." The substance here named "alkali blue" is known by British manufacturers as "Nicholson blue." The translator also tells us of "compounds which *go into* the corresponding phenol dyes when boiled with water." "Pass into" would have been a more idiomatic expression.

CORRESPONDENCE.

THE IODINE ABSORPTION OF ESSENTIAL OILS.

To the Editor of the Chemical News.

Sir,—I exceedingly regret that I should have given the Editor of the *Chemist and Druggist*, and through him the readers of that publication, the slightest pretext for thinking that I have copied anything from his article on essential oils published in the issue of Oct. 19; nothing could possibly be further from my intention, and were it not for the innuendo cast upon my integrity by the note in last week's *Chemist and Druggist*, I should have considered it quite unnecessary to mention the fact that I had not seen the article of the 19th ult. until this morning.—I am, &c.,

R. A. Cripps, F.I.C.

Birmingham, Nov. 26, 1889.

WATER ANALYSIS.

To the Editor of the Chemical News.

Sir,—In an article on Water Analysis, by Mr. H. M. Vernon (Chemical News, vol. lx., p. 249), there occur several erroneous statements with reference to my process of water analysis, which I will thank you to allow me to correct.

1. I never evaporated water down, for combustion of the residue, in a *platinum* dish. The irregularities of the surface of such a dish would prevent, or render extremely difficult, the removal of the residue. The evaporation has always been performed in a glass dish.

2. The evaporation of a litre of water takes, at the most, eighteen hours, and not two days. It is the custom in my laboratory to begin the evaporation in the afternoon, and the dry residue is then ready for combustion at 10 o'clock on the following morning. That there is no access of dust, as alleged by Mr. Vernon, is, I think, proved by the fact that when the operations were removed from London to the much purer air of Reigate, no effect of the kind was perceptible.

3. I have never admitted, as alleged, that "nitrogenous organic impurities in the water" are decomposed and lost during evaporation; and, consequently, I have never "drawn up tables" showing the amount of such loss. I have drawn up tables showing the loss of ammonia during evaporation, but this loss has nothing whatever to do with organic matter; and the quantity of ammonia in potable waters is very rarely large enough to require any correction on this score. The tables are chiefly of use in the analysis of sewage and foul waters.

Had Mr. Vernon tried the process of evaporation *in vacuo* which he suggests, he would not have recommended it. I tested it thoroughly more than twenty years ago, and abandoned it as impracticable and affording no advantage.—I am, &c.,

E. Frankland.

The Yews, Reigate
Nov. 26, 1889.

IODINE VALUES OF OILS AND FATS.

To the Editor of the Chemical News.

SIR,—Seeing that the process known as the "iodine absorption" is mentioned in connection with the analysis of essential oils, may I be allowed to point out the importance of having a large excess of the reagent present? Neglect of this precaution renders results obtained by this test nearly, if not altogether valueless, and is not improbably the cause of many of the discrepancies between various observers.—I am, &c.,

J. A. WILSON.

Tottington, near Bury, Lancashire,
December 2, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

NOTE.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 20, November 11, 1889.

The Incineration of Vegetable Matters.—G. Lechartier.—This paper will be inserted in full.

Simultaneous Solubility of Potassium and Sodium Chlorides.—A. Etard.—The author's experiments are summarised in the form of a diagram.

An Application of Thermo-Chemistry.—Alb. Colson.—It is tedious and difficult to demonstrate the identity or the dissimilarity of the alkaline functions in a polybasic alkaloid by the ordinary procedures of pure chemistry. In the case of nicotin, thermo-chemistry rapidly yields precious indications, which lead to the admission of dissymmetry in the constitution of this alkaloid.

No. 21, November 18, 1889.

Animal Heat and the Formation- and Combustion-Heats of Urea.—M. Berthelot and P. Petit.—In order to apply the author's rules and calculations, and to define accurately and in detail the production of animal heat, it is necessary to know the individual heat of formation and combustion of each of the compounds which intervene in alimentation, as well as that of each of the products eliminated by different channels.

Researches on the Application of the Measure of Rotatory Power to the Study of the Combinations Resulting from the Action of Malic Acid to Sodium Molybdate.—D. Gernez.—This paper is not adapted for useful abstraction.

Moniteur Scientifique, Quesneville.
Series 4, Vol. iii., October, 1889.

Aniline Black and the Grawitz Processes.—This unfortunate controversy is still raging, and not merely experts, but courts of judicature, are giving contradictory decisions.

Falsifications of the Vegetable Oils of Commerce.—P. J. S. Girard.—The conclusion of this long and important monograph.

Manufacture of Ammonia.—Mr. Ludwig Mond.—From the *Journal of the Society of Chemical Industry*.

Improvement in the Manufacture of Sulphuric Acid.—F. Benker.—A new arrangement of towers to effect the more rapid condensation of the acid vapours. These are square or oblong towers of stoneware filled with a number of perforated plates of the same material. It is expected that these towers will shortly be substituted for the Gay-Lussac coke-towers.

Indian Ink.—B. Piffard.—From the CHEMICAL NEWS.

New Apparatus destined for the Analysis of Oils.—F. Jean.—This paper requires the four accompanying cuts.

The Great Chemical Industries at the Paris Exhibition of 1889.—P. Kienlen.—This paper treats exclusively of the manufacture of sulphuric acid, and concludes with the judicious wish that the use of an instrument so irrational as Baumé's may be abandoned.

A New Reagent for Cane-Sugar, Grape-Sugar, and Pyrogallic Acid.—Matthieu Plessy.—This reagent is a solution of lead paranitrate in melted ammonium nitrate, in which the pulverised lead nitrate is first dissolved. When nearly dissolved it is withdrawn from the fire and powdered litharge is added. The proportions are 45 parts ammonium nitrate, 34 parts lead nitrate $(NO_3)_2Pb$, and 21 parts lead oxide. This substance is cautiously melted by heat and a small quantity (0·005 grm.) of the substance in question is added, which gives a characteristic colouration, With glucose there is obtained a cherry-red colour. The substance is added before the complete fusion of the lead salt, the tube is withdrawn from the heat, and well shaken in an inclined position. For saccharose the lead salt is completely melted, the sugar is added, and the heating is continued until a *café au lait* colour appears. For pyrogallic acid sample is mixed with the solid salt, the whole is melted and heated until a chrome green appears.

Note on Turkey Red.—G. Saget.—Turkey red being a double alizarate of aluminium and calcium, it was interesting to know if the calcium could be replaced by another metal of the same atomicity, and what would be the tone of these new double salts. The use of any calcareous salt was carefully avoided. The alizarin was that for violets, and the metals were introduced into the dye-beck in the state of pure carbonates. Compared with a normal turkey red, the tones obtained were:—Barium, bluish red verging to crimson; strontium, red, slightly bluish; magnesium, bluish red-brown; manganese, yellowish red-brown; zinc, light garnet brown; nickel, light garnet violet; copper, dregs of violet; lead, light garnet red. The strontium red comes nearest to ordinary turkey red. All these double alizarates are equally fast.

Fermented Milk.—Ad. Tscheppe.—From the *Pharmaceutical Journal*.

Fatal Poisoning with Carbon Monoxide.—Prof. W. Mason.—From the CHEMICAL NEWS.

MEETINGS FOR THE WEEK.

MONDAY, Dec. 9th.—Medical, 8.30.
— Society of Arts, 8. (Cantor Lectures). "Modern Developments of Bread-making," by William Jago.
TUESDAY, 10th.—Institute of Civil Engineers, 8.
— Royal Medical and Chirurgical, 8.30.
— Photographic, 8.
WEDNESDAY, 11th.—Society of Arts. "The Paris Exhibition," by H. Trueman Wood, M.A., Secretary to the Society.
— Microscopical, 8.
— Pharmaceutical, 8.
— Sanitary Institute, 8. "The Disposal of Sewage," by W. Santo Crimp, Assoc.M.I.C.E.
THURSDAY, 12th.—Royal, 4.30.
— Mathematical, 8.
— Institute of Electrical Engineers, 8.
FRIDAY, 13th.—Astronomical, 8.
— Quekett Club, 8.

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THE CHEMICAL NEWS.

Vol. LX. No. 1568.

CONSTITUTION OF BASIC SALTS AS EXEMPLIFIED BY A COMPARISON OF CERTAIN NITRATES AND PHOSPHATES.

By GEORGE WATSON, F.C.S.

Having had occasion some time ago to work at various methods of manufacturing pure phosphoric acid in large quantities, the common method of oxidation of phosphorus by hydric nitrate was tried amongst others, and during the experiments with it the analogies discussed below suggested themselves.

When phosphorus is heated with dilute hydric nitrate of sp. gr. about 1·200 it gradually disappears, evolving at the same time bubbles of a colourless gas which do not redden on admixture with air. This gas must, consequently, be either nitrous oxide or nitrogen. From some of my own experiments I am inclined to think that it consists of nitrogen in some cases, but as I have not yet proved this by direct experiment it may be assumed, for the basis of what follows, to be nitrous oxide. Then, inasmuch as burning phosphorus reduces this gas to nitrogen, we may imagine the phosphorus to be divided into two parts, one evolving nitrous oxide from the dilute nitric acid, the other burning in the nitrous oxide produced and forming nitrogen therefrom. Hence the operation may be viewed as a substitution of phosphorus for the nitrogen in nitric acid. Or it may be looked at in this way. As phosphorus burns in nitrous oxide, forming nitrogen, it should likewise burn in the more oxygenated compound, nitric oxide. This it is known to do; therefore it will burn in the highly oxygenated compound, gaseous hydric nitrate (HNO_3), displacing therefrom nitrogen. If, then, we imagine the substitution to be carried out with the latter substance, there will be formed the phosphorus analogue of HNO_3, viz., metaphosphoric acid. The substance symbolised HNO_3 may therefore be termed metanitric acid. If the substitution be performed in a mixed vapour of hydric nitrate and water, in the proportion $HNO_3 + H_2O$, there will be formed orthophosphoric acid. The hydrate HNO_3, H_2O, or H_3NO_4 is therefore analogous to orthophosphoric acid, and may be termed orthonitric acid. In the same manner, by substituting phosphorus for nitrogen in the vapour of $2HNO_3+H_2O$ we get $H_4P_2O_7$. Hence this hypothetical or unisolated hydrate is analogous to pyrophosphoric acid.

Taking these two series of acids, and forming metallic derivatives from them by substituting a divalent metal, we get as follows:—

Nitric Series.

HNO_3 —	$M''(NO_3)_2$	1.
$H_4N_2O_7$ —	$M''H_2N_2O_7$ or $M''(NO_3)_2H_2O$	2.
	$M''_2N_2O_7$ or $M''(NO_3)_2M''O$	3.
H_3NO_4 —	$M''HNO_4$ or $M''(NO_3)OH$	4.
	$M''_3(NO_4)_2$ or $M''(NO_3)_22M''O$	5.

Phosphoric Series.

HPO_3 —	$M''(PO_3)_2$	1.
$H_4P_2O_7$ —	$M''H_2P_2O_7$	2.
	$M''_2P_2O_7$	3.
H_3PO_4 —	$M''HPO_4$	4.
	$M''_3(PO_4)_2$	5.

Leaving on one side the phosphoric series of salts, and looking at the nitric series only, it is seen that, with the exception of Nos. 1 and 2, the other salts are basic nitrates of a divalent metal. Basic salts, corresponding to monobasic orthonitrates, have been prepared containing lead, zinc, cadmium, mercury (*ous* and *ic*) (*vide* Roscoe and Schorlemmer, "Treatise on Chem.," and H. Klings, *Ber.*, xvi., 997—999). Of normal pyronitrates, salts are said to have been isolated containing zinc and cadmium (H. L. Wells, *Amer. Chem. Jour.*, ix., 304—308), while a basic salt corresponding to triplumbic orthonitrate has also been prepared.

Dr. Perkin has recently adduced experimental evidence tending to prove the existence of orthonitric acid (*Proc. Chem. Soc.*, 1889, p. 130). Hence there is some reason for saying that all the basic nitrates which agree in formulæ with those required by the salts of this acid are not basic salts at all, but are in reality acid or normal orthonitrates, as the case may be; and the existence of orthonitric acid being in a measure proved, the probability of the existence of pyronitric acid is consequently increased. Whence, there also follows some reason for ceasing to view the salts of this acid as basic nitrates, and for looking at them as perfectly normal salts. And if this view be taken in the case of basic nitrates, may we not go a step further and view all basic salts as the normal or acid salts of hitherto unisolated hydrates of their respective acids? Professor Pickering has at various times promulgated the hypothesis that basic salts are strictly analogous to the hydrates of acids which exist in solution, and if it be agreed to view the various hydrates of a given acid as individual acids, differing from each other in the manner, although probably not in the degree, that the three acids of phosphorus differ from each other, then, I think, that the hypothesis becomes more significant. The term "basic salt" would then cease to have any special meaning, and all such salts could be ranged in the two groups of acid or normal salts, or, to speak more correctly, of partially and wholly substituted acids.

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DANGER FROM THE USE OF NATURAL GAS.

By F. MAXWELL LYTE, F.C.S., F.I.C.

It is worthy of consideration what will be the effect on the strata from which the natural gas which serves as the principal combustible in many parts of the United States is derived, as soon as it has all been used up and when it falls to the ordinary atmospheric pressure. This must assuredly take place sooner or later, and probably at no very distant period considering how rapidly the gas is being squandered. In the calculations below, the data on which they are founded are as follows:—

1. The average pressure at which the gas issues from the wells is said to be about 200 lbs. to the square inch = 28,000 lbs. to the square foot.

2. An acre contains 43,560 square feet.

3. A square mile contains 640 acres.

From these may be calculated the supporting pressure by which the overlying strata must at present be upheld from below.

Unless I am mistaken the gas would give a pressure which, for each square mile, would amount to no less than 358,436,571 tons, equivalent to the weight of a fair-sized mountain; so that on its ceasing to issue, proving thereby that the supporting pressure was withdrawn, the superincumbent strata would necessarily tend to give way. While the gas was there at so great a pressure there must have been an enormous pressure upwards, and when it disappeared this would probably be replaced by a still greater strain downwards.

The strata are already unable to support their own

weight even over a limited area: witness the serious depressions occurring in many places over abandoned coal mines, and the numerous subsidences which are continually taking place in the salt districts, and most of the natural gas has been obtained from similar formations to these. Supposing the gas to be derived from reservoirs of gaseous hydrocarbons which have been liquefied by pressure, these reservoirs must have an unknown depth and area. If the area be small no danger need be apprehended, from the great depth at which they are situated; but if large, as is probably the case, we, or our children, may yet be called on to witness such a dire and frightful catastrophe as the world has never seen, which would dwarf into insignificance the most terrible earthquake that ever happened. That the size of such reservoirs must be very considerable may be concluded from the persistency with which the gas is disengaged always at the same pressure, and from the constancy of its composition. If the strata were to give way the accident would probably be sudden, unexpected, and extensive. Very possibly, then, the inhabitants of those towns who draw their supplies of natural gas from the ground below them may be unwittingly working their own destruction by the use of this combustible, and while reposing in a fancied security, they may be preparing for themselves an abyss ready to swallow them up with scarcely a moment's warning. Let us hope that these fears are unfounded, for the calamity is one that is almost too terrible to be contemplated. If others more in a position to investigate the matter, after considering what I have said, should agree with me as to the probability or even the possibility of the truth of my previsions, better at once close all the gas wells, or anyway those which could possibly endanger any town, while there is yet time, and revert to the use of coal, of which America possesses such abundant supplies, than run the chance of a disaster such as I here foreshadow.

OSMOTIC PRESSURE:

With Special Reference to the Work of Rüdorff and Raoult.*

By EMILY J. LLOYD.

Osmotic† pressure is the influence which bodies in solution exercise upon their solvents, causing alternation in the boiling-, freezing-, and maximum density-points. From the laws which govern these phenomena the molecular weights of the dissolved substance can, it is claimed, be determined.

The fact that a mixture of salt and water freezes at a lower temperature than pure water has long been known, and a paper by Blagden on this subject appeared in the *Phil. Trans.*, for 1788. But the first investigations of any importance were those of Fr. Rüdorff, published in *Poggendorff's Annalen* for 1861. His method of working was the following:—

A quantity of the pure salt was dried, weighed, and dissolved in 100 grms. water. The vessel, with its thermometer and stirrer, was then placed in a freezing mixture and stirred constantly (to prevent formation of ice on the surface, and consequent inequality of temperature). When the solution had fallen to some 0·3° or 0·5° below the expected freezing-point, a particle of snow was thrown in. Immediately flakes of ice appeared in all parts of the liquid. Simultaneously the thermometer rose. As in freezing water or melting snow the thermometer remains constant till all the water is frozen or all the snow melted, so, in this case, the thermometer remained stationary, till the quantity of ice was sufficient to affect the unfrozen solution; then it began to sink. The stirred up liquid was then removed from the freezing mixture, and the thermometer rose till the melting-point was reached; there it was stationary till the ice disappeared. The melting-point was found to be the same as the freezing-point.

An experiment with common salt gave the following:—

After being in the freezing mixture—	The thermometer marked—
0′	−0°
1′	−1°
2′	−1·5°

Ice then began to form, and the thermometer rose to −1·2°; it remained at that temperature *for thirteen minutes*, then it fell slowly till, at the end of six minutes more, it stood at −1·5°. The solution was then removed from the freezing mixture. In three minutes the thermometer had risen to −1·2°, at which temperature it remained *for twenty-two minutes*; then it rose again till the ice was fully melted. That this temperature, −1·2°, may be regarded as the true freezing-point or melting-point of the liquid is sufficiently manifest.

The following Tables give the values of Rüdorff's first experiments.

M = Number of grms. of salt in 100 grms. water.

T = Temperature to which the freezing-point of the solution was lowered below the zero, C.

Sodium Chloride.

M.	T.	$\frac{T}{M}$
1	−0·6	−0·600
2	−1·2	−0·600
4	−2·4	−0·600
6	−3·6	−0·600
8	−4·8	−0·600
10	−6·0	−0·600
12	−7·2	−0·600
14	−8·4	−0·600
Mean =		−0·600

Potassium Chloride.

M.	T.	$\frac{T}{M}$
1	−0·45	−0·450
2	−0·90	−0·450
4	−1·80	−0·450
6	−2·65	−0·442
8	−3·55	−0·443
10	−4·40	−0·440
12	−5·35	−0·446
Mean =		−0·446

Sodium Sulphate.

M.	T.	$\frac{T}{M}$
1	−0·3	−0·300
2	−0·6	−0·300
3	−0·9	−0·300
4	−1·15	−0·290
Mean =		−0·297

Potassium Sulphate.

M.	T.	$\frac{T}{M}$
2	−0·4	−0·200
4	−0·8	−0·200
6	−1·2	−0·200
8	−1·65	−0·206
Mean =		−0·201

Potassium Bromide.

M.	T.	$\frac{T}{M}$
4·74	−1·40	−0·295
11·16	−3·25	−0·291
19·82	−5·75	−0·290
31·10	−9·00	−0·290
Mean =		−0·292

Potassium Iodide.

M.	T.	$\frac{T}{M}$
3·76	−0·80	−0·213
10·34	−2·20	−0·212
26·24	−5·55	−0·211
58·15	−12·25	−0·211
Mean =		−0·212

So with other salts.

	$\frac{T}{M}$ =
For ammonium chloride	−0·653
,, ammonium nitrate	−0·384
,, sodium ,, ...	−0·370
,, potassium ,, ...	−0·267
,, calcium ,, ...	−0·277
,, potassium carbonate	−0·317
,, calcium ,, ...	−0·277

Here we notice:—

1. The lowering of the freezing-point is greater, the greater the amount of salt dissolved.

* A Paper read before the Mason College Chemical Society, October 16, 1889.

† The word "osmotic" is derived from the Greek ὠσμος, a thrusting.

2. The quotient

$$\frac{T}{M}$$

shows that the lowering of the freezing-point for each grm. of salt dissolved is constant for each salt.

During the next two years, Rüdorff investigated the freezing-points of solutions of several other salts; chlorides of copper, barium, strontium, calcium, magnesium, cobalt, and nickel; sulphates of potassium, ammonium, magnesium, manganese, zinc, and copper; nitrates of sodium, nickel, and strontium; hydrates of potassium, sodium, ammonium; hydriodic, sulphuric, and nitric acids; and sulphocyanate of potassium.

The results were not always concordant, as in the previous cases. Frequently the quotient

$$\frac{T}{M}$$

showed an increasing number.

Thus, with the chlorides of calcium and manganese :—

Calcium Chloride.			*Manganese Chloride.*		
M.	T	$\frac{T}{M}$	M.	T.	$\frac{T}{M}$
1	−0·40	−0·400	4·03	1·00	−0·248
2	−0·90	−0·450	4·25	1·05	−0·247
4	−1·85	−0·462	9·72	2·45	−0·252
6	−2·85	−0·476	19·70	5·55	−0·282
8	−3·90	−0·487	33·88	10·85	−0·320
10	−4·90	−0·490	36·58	11·55	−0·330
14	−7·40	−0·528			
18	−10·00	−0·555			

Moreover, the solutions of common salt containing more than 14 grms. of salt to 100 grms. water are irregular :—

M.	T.	$\frac{T}{M}$
15	−9·2	−0·613
16	−9·9	−0·619
17	−10·6	−0·623
18	−11·4	−0·633
19	−12·1	−0·637
20	−12·8	−0·640

But a salt $NaCl2H_2O$ is known, and is shown by Mitscherlich to crystallise out below −8°. Calculated for this salt

$$\frac{T}{M}$$

becomes constant. The Table becomes :—

M.	T.	$\frac{T}{M}$
26·70	−9·2	−0·345
28·67	−9·9	−0·345
30·67	−10·6	−0·346
32·70	−11·4	−0·349
34·76	−12·1	−0·348
36·84	−12·8	−0·347
	Mean =	−0·347

This seems to indicate an abrupt change.

De Coppet, who criticised and repeated Rüdorff's experiments, gave the following results of experiments on this salt :—

M = Weight of salt considered anhydrous.

M_2 = Weight of salt considered combined with $2H_2O$.

M.	M_2.	T.	$\frac{T}{M}$	$\frac{T}{M_2}$
5	8·33	−2·9	−0·580	−0·348
10	17·31	−6·1	−0·610	−0·354
15	26·69	−9·7	−0·647	−0·363
17·5	31·68	−11·45	−0·654	−0·361
20·0	36·85	−13·6	−0·680	−0·369
21·87	40·82	−15·05	−0·688	−0·369
29·16	57·40	−21·4	−0·734	−0·373

Numbers which, he says, show that a hydrate is gradually formed. Despretz and Rosetti, in their work on the density of solutions, came to the same conclusion.

Rüdorff goes on, in his paper, to say :—"The question is : In these salts, where

$$\frac{T}{M}$$

is an increasing ratio, will the relation be constant if we take the salt in the solution as combined with more molecules of water?"

Let r denote the number of water equivalents with which the anhydrous salt unites in the solution.

M, the number of grms. of anhydrous salt dissolved in 100 grms. water.

A, the equivalent of the same.

S, the quantity dissolved in 100 grms. water.

Then, manifestly—

$$S = \frac{(A+18r)\,M \times 100}{100\,A - 18r\,M} \quad . \quad . \quad . \quad . \quad (I.)$$

From similar observations we can show a relation between M′ and S′.

$$S' = \frac{(A+18r)\,M' \times 100}{100\,A - 18r\,M'} \quad . \quad . \quad . \quad . \quad (II.)$$

If t and t' be temperatures corresponding to S and S′ we have, further,—

$$S : S' = t : t',$$

or,—

$$St' = S't \quad . \quad . \quad . \quad . \quad . \quad (III.)$$

Eliminating S and S′ between these three equations we find—

$$r = \frac{100\,A\,(Mt' - M't)}{18\,M\,M'\,(t - t')} \quad . \quad . \quad . \quad . \quad (IV.)$$

(where already there are n molecules of water—

$$r = \frac{(100\,A + 18n)\,Mt' - M't)}{18\,M\,M'\,(t' - t)}\Big)$$

If we apply this equation to the numbers in the above Table for manganese chloride, we find $r = 12$ and

$$\frac{T}{M}$$

becomes—

−0·139
−0·139
−0·136
−0·139
−0·138
−0·138

The correction was applied by Rüdorff to some 45 other salts (*Pogg. Ann.*, 145).

For example, Sr, Co, Ni, Mn, chlorides; Mg, Sn, Mn, Ni, Cd, and Cu, nitrates, he finds are combined with 12, sulphates of Mg, Zn, and Ni with 7 molecules of water, and so forth.

From the preceding, Rüdorff drew the following conclusions :—

1. In aqueous solutions the freezing-point of the solution is lowered proportionally to the amount of salt dissolved.

2. Some salts lower the freezing-point when free from water.

3. Others behave as hydrated salts.

4. Others, again, lower the freezing-point as non-hydrated to a certain temperature, then as hydrated salts.

5. Hence it follows that the investigation of the freezing-point offers a means of deciding whether a salt is free from water, or is united with water in the solution.

The case of copper chloride is interesting :—The green colour of the solution at a certain stage changes to blue; corresponding to the change of colour is an irregularity in the value of

$$\frac{T}{M}.$$

Where M is less than 16 grms. in 100 grms. of water the green colour obtains, and calculation gives $r=4$; where M is greater than 20 (the change of colour takes place gradually between these two numbers), $r=12$. Hence, Rüdorff concludes that the green solution contains the salt $CuCl_24H_2O$, and the blue solution, $CuCl_212H_2O$.

Rüdorff next investigated the case of some double salts which for the quotient

$$\frac{T}{M}$$

gave decreasing values. Applying the formula (IV.) given above he found $r=-6$, and hence, concluded that these salts, though in the solid form combined with six molecules of water, dissolve in water as anhydrous salts, their water of crystallisation being added to the solvent water.

In 1871 and 1872, De Coppet published, in the *Annales de Chimie et de Physique*, lengthy criticisms on Rüdorff's paper, and compared his results with those arrived at by Despretz in his paper on the points of maximum density.

De Coppet examined a number of salts of the alkalies and alkaline earths, and concluded that in some cases the salt is partially decomposed in solution — but he added to the coincidences worked out by Rüdorff, the following important fact :—

In the case of KCl, KBr, and KI, *if the quotient*

$$\frac{T}{M}$$

be multiplied by the molecular weight of the salt in question, the product is approximately the same in the three cases :—

For KCl	.. .. ..	0·455 ×	74·6	= 33·9
,, KBr	.. .. ..	0·292 ×	119	= 34·8
,, KI ..	.. .. ..	0·212 ×	166	= 35·2

In other words :—

An equal number of molecules of chloride, bromide, and iodide lowers the freezing-point approximately the same number of degrees.

This quantity,

$$\frac{T}{M} \times A,$$

De Coppet calls the *atomic depression* of the freezing-point.

$$\frac{T}{M}$$

he calls the *coefficient of depression.*

(To be continued).

THE INCINERATION OF VEGETABLE MATTER.

By G. LECHARTIER.

The incineration of vegetable matter is a delicate operation when we wish to avoid any loss of the mineral matter by mechanical dispersion or by volatilisation. Under various circumstances special precautions have been observed. M. Schlœsing first effects the slow carbonisation of the substance in an atmosphere of carbonic acid, and then burns the carbon by means of oxygen. M. Berthelot conducts the combustion in a current of oxygen, passing the products through a column of sodium carbonate heated to dull redness.

These precautions seem to regard losses as possible. The author therefore thinks it useful to inquire if losses may be avoided in incinerations in the open air, and to determine what is their amount in cases where they necessarily occur. This question is interesting, not merely for future investigations, but also concerning former researches emanating from distinguished *savants* whose name carries authority.

In every incineration we may distinguish two principal facts :—

1. Carbonisation of the vegetable matter, with disengagement of watery vapour, tar, gaseous hydrocarbons, and various volatile products.

2. Partial combustion of the vapours and complete combustion of the carbon, which still forms part of every fragment of the matter after the complete disappearance of everything volatile. During this last part of the process the phosphates are exposed to more or less elevated temperatures in contact with carbon and in presence of silica.

The author has studied the two phases of the process separately. He has incinerated grains of wheat and buckwheat, entire plants, wheat cut at the time of flowering, tubers of Jerusalem artichoke, and the straw of buckwheat. Forty to fifty grms. of the substance were operated upon at once.

1. *Carbonisation of the Vegetable Matter.*—This process was effected in a small platinum retort, the head of which was adjusted to the body by simple rubbing. The neck of the retort was connected by a cork to a refrigerated receiver, the second tubulure of which communicates with a bulb-tube containing strong nitric acid. A regular aspiration is kept up in the apparatus by means of a water-sprengel to prevent any excess of pressure and loss of vapours at the point of junction of the head and body. The retort is heated by means of a strong Bunsen burner, the flame of which is gradually raised so as to bring the matter gradually to redness. At the end of the operation a temperature is reached higher than is required for incinerations in the open air. The liquids condensed are evaporated with the nitric acid after the addition of pure lime. The product of the evaporation is ignited to destroy the tar. After re-dissolving in water and nitric acid he pours into half the liquid an acid solution of ammonium molybdate, and into the other half a solution of barium nitrate.

The liquid contained in the bulb tube is submitted to an identical operation.

In every case a precipitate of barium sulphate is obtained. Most frequently there is no formation of a yellow precipitate of ammonium phosphomolybdate. In the cases when some trace of a precipitate is formed it is redissolved in ammonia and magnesium nitrate is added, but the ammonium-magnesium phosphate is not precipitated on taking the results of a single operation.

The molybdic precipitates obtained in six successive experiments were collected when the ammonium-magnesium phosphate became appreciable; it yielded 0·001 grm. pyrophosphate for a quantity of matter corresponding to 120 grms.

The precipitates of barium sulphate corresponded to weights of sulphur ranging from 11 to 54 m.grms. in 400 grms. of the vegetable matter.

These experiments were varied as regards the phosphorus. In a second series of experiments the platinum tube was placed in connection with a tube containing a column of sodium carbonate followed by a column of quicklime. The sodium carbonate was heated to incipient redness and the lime to bright redness. The tube was followed by a condenser and this again by a tube containing nitric acid. In the carbonisation of 80 grms. of wheat, 1 m.grm. of phosphoric acid was extracted from the matter condensed in various parts of the apparatus, but it is not certain that nothing was carried away mechanically.

2. *Combustion of Carbon.*—Grains of wheat previously carbonised were heated in a current of oxygen, and the gases were passed over a column of lime raised to bright redness. The lime when dissolved did not yield a trace of phosphoric acid. The operation was performed on 25 grms. of wheat.

3. In *mixed experiments*, where the carbonisation was followed by incineration, more or less prolonged, no phosphoric acid was found in the volatile matters,

whether they were condensed in a receiver or passed over sodium carbonate heated to dull redness.

4. Lastly, it seemed useful to determine the phosphoric acid in one and the same vegetable:—(1) On incinerating in oxygen in a tube containing a column of sodium carbonate; (2) on incinerating in a platinum capsule in the air; (3) on incinerating after having moistened with milk of pure lime at 5 per cent and drying; (4) using a solution of calcium nitrate containing an excess of lime. This solution does good service in incinerating organic manures; but with grain it may occasion deflagration with loss of matter.

The proportion of phosphoric acid found in 100 parts of wheat (grain only) was, on incineration in oxygen, 0·770; in the open air, without addition, 0·767; in presence of lime, 0·770; and in presence of sodium nitrate (? calcium nitrate), 0·780.

The slight differences found in these results are within the possible limits of experimental error and of the variations of composition which may occur in two samples of the same vegetable.

In fine, in the carbonisation and incineration of a vegetable there is a notable loss of sulphur volatilised in different combinations, a part of which may be condensed in a liquid state. Special precautions are necessary for determining the sulphur.

Under the same conditions, if all carrying off solid matter by the escaping vapours and gases is prevented there is no appreciable loss of phosphorus.

The incinerations in the air were effected as follows:—The platinum capsule containing the substance is placed on a piece of tile which is heated in a gas-furnace. The capsule is covered with an inverted gas-funnel, which is kept slightly raised above the capsule. The heat is applied gradually, beginning with the smallest possible flame, so as to produce a slow escape of vapours and gas. When this escape ceases the bottom of the capsule is raised to nascent redness for a few moments, so as to complete the decomposition of the vegetable matter. The carbon is washed with hot water, decanting the liquid over a paper filter; three or four washings with a small quantity of water are sufficient. The filter, with its contents, is introduced into the capsule, dried, and heated to dull redness, when the incineration is rapidly effected. The liquid from washing the carbon is added to the ash, evaporated to dryness, and weighed; or the residue is treated with nitric acid.

If this treatment with nitric acid shows small particles of carbon they are filtered off and incinerated, adding their ash to the rest of the matter. This carbon still contains phosphoric acid, notwithstanding the acid washings.

For determining the phosphoric acid it is advantageous to mix the substance intimately with milk of lime sufficient to moisten all its parts. The mixture is dried and ignited. —*Comptes Rendus* (Vol. cix., p. 727).

ISOMERIC NAPHTHALENE DERIVATIVES.*

The study of naphthalene derivatives has been prosecuted in the reporter's laboratory during the past year with far greater success than could have been anticipated, chiefly owing to the untiring energy and skill of Mr. W. P. Wynne; valuable assistance having also been rendered by several students. The results are, it is believed, of considerable importance from a theoretical point of view, not merely in relation to naphthalene derivatives, but in connection with the general problem of the nature of the changes involved in the production of isomeric compounds.

Constitution of the Isomeric Dichloronaphthalenes.—A list of the twelve reputed dichloronaphthalenes was given in the last Report, and their constitution was provisionally discussed. The results since obtained render it possible to finally assign the proper formulæ to the several modifications, the method adopted affording almost, if not quite, as absolute a determination of their constitution as that employed by Körner in the case of the dibromobenzenes: an account thereof is given in the *Proceedings of the Chemical Society*, 1888, pp. 104—107; 1889, pp. 34—37; pp. 48—54. The conclusions arrived at by Erdmann and Kirchhoff are confirmed; as the synthetic method which these chemists had adopted was one which did not exclude the possibility of the occurrence of isomeric change, objection was taken to their proof in the last Report, but it is now clear that they had correctly interpreted their results.

The so-called α-dichloronaphthalene, m. p. 38°, obtained by the action of alcoholic potash on naphthalene tetrachloride, has been proved to be a mixture of 1:4 (β) dichloronaphthalene, m. p. 68°, and 1:3 (θ) dichloronaphthalene (m. p. 61°) (*cf. Chem. Soc. Proceedings*, 1888, 106). It has previously been pointed out that the so-called κ-dichloronaphthalene of Claus has no claim to recognition, and that it is doubtful whether the ι-dichloronaphthalene described as melting at 120° was a pure substance; consequently at present but nine of the ten possible dichloronaphthalenes are to be regarded as beyond doubt existent; their constitution is as follows:—

		M. p.	Position of radicles.
αα.	Modifications:—		
	β. Dichloronaphthalene..	68°	1:4
	ζ. ,, ..	83°	1:1′
	γ. ,, ..	107°	1:4′
ββ.	Modifications:—		
	δ. ,, ...	114°	2:2′
	ε. ,, ...	135°	2:3′
αβ.	Modifications:—		
	— ,, ...	34°	1:2
	θ. ,, ...	61° (about)	1:3
	θ′. ,, ...	63° ,,	1:2′
	η. ,, ...	48°	1:3′

The Alpha-law. Spontaneous occurrence of Isomeric Change on Sulphonation.—In previous reports attention has frequently been directed to the circumstance that, as a rule, *alpha*-derivatives are formed, and that *beta*-derivatives are only obtained either when a group is present in an alpha position, which determines the entry of the new group into the contiguous beta position, or owing to the occurrence of secondary change; it has, in fact, been argued that an isolated beta position is never directly attacked. Further evidence, tending to strengthen this conclusion, has recently been obtained. When either β-chloro- or β-bromonaphthalene is sulphonated, the chief product is the 2:1′ α-acid; and a relatively very small amount of the isomeric 2:3′ β-acid is also obtained, and it was suggested that this was formed by spontaneous isomeric change from the 2:1′ acid, as it was found possible to convert the α- into the β-acid by heating. β-Iodonaphthalene, in like manner, was found to yield two sulpho-acids, but it was pointed out in the second of these reports that the melting point of the sulphochloride of the acid found in small quantity was remarkably low. Recent experiments of Mr. Houlding (*cf. Chem. Soc. Proc.*, 1889, 74) have served to show that the minor product is not the 2:3′ derivative. Subsequently, Mr. Wynne and I have found (*ibid.*, 1889, 119) that the chief product of sulphonation in the case of β-iodonaphthalene corresponds with the chief product afforded by β-chloro- and β-bromonaphthalene, and that the minor product obtained from β-iodonaphthalene is the second heteronucleal 2:4′

* Fourth Report of the Committee, consisting of Professors Tilden and Armstrong (Secretary), appointed for the purpose of investigating Isomeric Naphthalene Derivatives. (Drawn up by Professor Armstrong). Read at the Newcastle-upon-Tyne Meeting of the British Association, 1889.

alpha-sulphonic acid: so that whereas only one alpha-acid is obtained on sulphonating β chloro- and β-bromo-naphthalene, β-iodonaphthalene yields the two possible heteronucleal alpha-acids. Both β-iodo α-sulphonic acids, however, are found to yield the same 2 : 3′ β-sulphonic acid when heated at about 150°. It is therefore not improbable that on sulphonating the chloro- and bromo-compounds, two *alpha* acids are initially formed, and that one of these forthwith undergoes spontaneous isomeric change into the 2 : 3′ acid.

The results obtained in the case of the dichloronaphthalenes tend to support this view. Thus, 1 : 3 (θ) dichloronaphthalene affords but a single sulphonic acid; this product is identical with that prepared by Widman from naphthalene-α-sulphonic acid, and is in all probability the 1 : 3 : 4′ acid.

1 : 2 dichloronaphthalene, however, yields two isomeric acids, the chief product (about $\frac{2}{3}$) being the 1 : 2 : 4′ (α) acid, the subsidiary product, the 1 : 2 : 3′ (β) acid; as the latter is almost the sole product if the original product of sulphonation be heated at 150°—160° during several hours, it is probable that the β-acid in the original product is formed by spontaneous isomeric change at the moment of sulphonation.

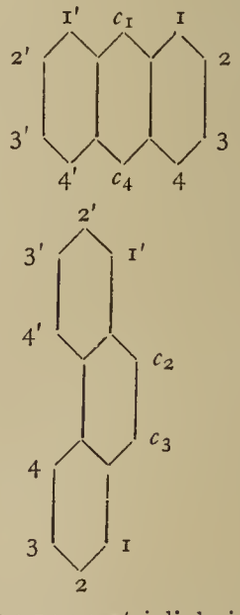
1 : 4 (β) dichloronaphthalene, however, yields as sole product the 1 : 4 : 2′ (β) sulphonic acid, and it would appear that isomeric change takes place in this case spontaneously and with exceptional facility and completeness.

1 : 4′ (γ) dichloronaphthalene yields as chief product (about four-fifths), the 1 : 4′ : 2′ beta-sulphonic acid (m. p. of sulphochloride 139°—140°), together with what appears to be the isomeric 1 : 4′ : 3′ beta-acid (m. p. of sulphochloride 98°—100°); in this case it is possible that an alpha-acid is first formed, which at once changes, but more probably the two alpha positions are "protected" by the two alpha-chlorine atoms, the 1 : 4′ : 3′ beta-acid being first formed, and at once partly converted by spontaneous isomeric change into the more stable 1 : 4′ : 2′ acid. It is obvious that much important information is to be obtained by further study of this subject.

Azo-Dye Stuffs Derived from Naphthalene.—In the second of these reports it was argued that the azo-dye stuffs from betanaphthol were all 1 : 2 α-β-derivatives, and, as a matter of course, the argument would apply equally to betanaphthylamine. Experiments were commenced with the object of obtaining the data required to verify this theory, but their continuance became unnecessary in consequence of the publication of a valuable paper by Dr. O. N. Witt (*Berichte*, 1888, 34—68), in which it is demonstrated that the azo-colours from the four isomeric betanaphthylaminesulphonic acids and a number of others are all 1 : 2 derivatives. In pointing out (*cf. second* report), that the formation of the azo-colour involves an isomeric change which apparently can take place only in the one direction, and that on this account it is impossible to effect the introduction of the azo-group into any other position than that contiguous to the OH or NH_2 group, no special note was taken of the peculiar constitution of the colouring matters themselves; the further study of this question, however, has led me to the conclusion that even if the transference could be effected in any other way, azo colours would only result provided that "quinonoid" compounds were formed; at present this is only known to obtain in the case of the 1 : 2 and 1 : 4 compounds (*cf. Chemical Society Proceedings*, 1888, p. 27).

The Symbol of Naphthalene.—There appears to be a tendency on the part of some recent investigators of naphthalene derivatives to consider that the naphthalene molecule is dissymmetric. Without discussing this question in detail I would express my conviction that this is not the case, and that the behaviour of naphthalene, and especially its characteristic tendency to form alpha-derivatives, may be satisfactorily expressed by means of a symbol similar to that which I have suggested for benzene (*Phil. Mag.*, Feb. 1888), viz.:—

Notation of Naphthalene Derivatives. — Throughout these reports, &c., the system of notation introduced many years ago by the Chemical Society and in "Watts's Dictionary of Chemistry" has always been made use of, and its general adoption was advocated in a recent paper by Mr. Wynne and myself (*cf. Chem. Soc. Proceedings*, 1889, p. 54). It consists in numbering the positions in the one nucleus 1, 2, 3, 4, and the corresponding positions in the second nucleus 1′, 2′, 3′, 4′. The practice of numbering the positions 1 to 8 appears less desirable and rational in view of the fact that naphthalene consists of two like nuclei, and of the importance of at once being able to recognise which are corresponding positions. In a recent conference at Paris it was, however, resolved to recommend the system of numbering the positions 1 to 8, but this decision appears to have been arrived at without any sufficient discussion of the question or pains being taken to consult those who have the right to express an opinion. The desirability of numbering corresponding positions similarly in all multinuclear compounds cannot be denied, and it is very easily carried into practice; thus in the case of phenanthrene the positions in the one *lateral* nucleus are 1, 2, 3, 4, in the other 1′, 2′, 3′, 4′, and in the *central* nucleus c_2, c_3; in the case of anthracene those in the central nucleus are c_1, c_4, those in the one *lateral* nucleus 1, 2, 3, 4, those in the other 1′, 2′, 3′, 4′. Thus:—



Anthraquinone is a 1 : 4 *centri*-di-derivative, phenanthraquinone a 2 : 3 *centri*-di-derivative.

Employment of Electric Conductivity for the Study of the Displacements and Distributions of Acids of Complex Functions.—Daniel Berthelot.—Aspartic acid is one of those bodies which unite an acid and an alkaline function. The author has undertaken to study the equilibria produced in the presence of this acid in dilute saline solutions. These equilibria depend on the presence of the antagonistic acids, which, on the one hand, may seize upon the whole or a part of the mineral base, and, on the other, may combine with the aspartic acid itself. The conductivities were measured by means of Lippmann's capillary electrometer.—*Comptes Rendus*, Vol. cix., No. 22.

THE INFLUENCE OF SILICON ON THE PROPERTIES OF STEEL.*

Continued from p. 275).

Outside, one might say even within, the laboratory the properties of the metalloid silicon, or silicium, are but little known. No fuller details can be found than in that part of Dr. Percy's work, "Metallurgy," relating to silicon, where all the methods for its production on a laboratory scale are given.

It is ordinarily described as a non-metal, very hard, dark brown in colour, a non-conductor of electricity, lustrous, not readily oxidised, and soluble in all ordinary acids with the exception of hydrofluoric. It is said to resemble carbon in its general properties. Others add that it exists, like carbon, in a graphitic, amorphous, and combined or adamantine form; but this is still to be determined.

Mr. Henry J. Williams, St. Louis, Missouri (U.S.A.), this year presented a paper to the American Institute of Mining Engineers on "The Determination of Silicon in Ferro-silicons: its Occurrence in Aluminium as Graphitoidal Silicon, and a Study of its Reactions with Alkaline Carbonates." As the latest investigation of this kind, it may be well to refer to the experiments. Mr. Williams's method of determining the metalloid was by means of fusion with sodium carbonate, the idea being to dissolve it as soluble sodium silicate, and leave the iron in a very spongy and finally divided condition so as to be readily attacked by acids. He noticed some curious facts during fusion. As soon as the sodium carbonate was thoroughly melted and the heat reached its maximum, the reaction became very violent, bubbles of gas (carbonic acid) rising to the surface and bursting into flame. This had been noticed before by another observer making experiments of similar nature with graphitic pig-iron. Mr. Williams was, however, somewhat puzzled, as the ferro-silicon with which he was experimenting was high in silicon and comparatively very low in carbon; yet it gave the same result. To ascertain why silicon acts exactly like carbon during the reduction, he endeavoured to obtain an iron entirely free from foreign elements, particularly carbon, but containing high silicon, but was unsuccessful. He found the desired condition realised in the aluminium of trade, most of which, in spite of its name, he states, contains not less than three per cent or four per cent of silicon, but of course no carbon. He found that a large part of the silicon in such aluminium seemed invariably present as an allotropic modification of that metalloid, crystallising in fine glistening black plates resembling some forms of graphite, and considered that this was evidently the graphitoidal form of silicon which Deville has mentioned in connection with aluminium, but which has not yet been isolated or found to exist in iron. Dr. Percy mentioned at length the same fact, and describes the material as resembling graphite from iron smelting furnaces, and as being hard enough to scratch glass, with a specific gravity of 2·49. As regards, however, the form silicon may take in cast-iron or steel, Mr. Keep considers that whether it exists in a state corresponding to graphitic carbon, and mechanically mixed with the remaining mass, is still a question in dispute. Mr. Holgate, of Darwen, also, in the paper before referred to, after making many analyses, says he has never found any evidence as to the existence of graphitic silicon in such alloys, though he has noticed some slight difference in the behaviour of silicon when dissolved in acids. Mr. Turner, in his paper some two years ago, after carefully investigating this point, both by means of xperiments of his own and those of Sir Frederick Abel, Mr. Snelus, and others, says that it may at any rate be considered, in a vast majority of cases at least, silicon has only one form. Finally, therefore, the practical metallurgist has at present, apparently, no means of readily determining this point, although he may have reason to think that silicon does vary its form in either cast-iron or steel.

In metallurgical literature but little information is to be found as to the effect of silicon upon iron. Mr. Howe, in his excellent work on "The Metallurgy of Steel," gives an excellent *résumé* of what has appeared. Some fourteen years ago in America good results were promised by a process which was to use "codorus or silicon ore," as it was termed. This was to dephosphorise or neutralise the phosphorus in the metal under treatment. Only a few years back the writer had reason to investigate this matter in America, but found that this so-called puddled silicon iron or silicon steel contained no silicon. The whole matter was well summarised by the well-known metallurgist, Holley, of America, who said, or rather sang of it,—

> There was an old man of Codorus
> Who said he took out the phosphorus,
> So the iron he puddled and with chemicals muddled,
> But the puddling took out the phosphorus.

Referring now to the consideration of silicon alloyed with the metal iron, the common belief has been that steel which has to be used in its forged state should contain practically none or as small an amount as possible. Any quantity exceeding 0·10 per cent, or up to 0·20 per cent at most, has been considered to be highly injurious. "Give a dog a bad name" is well illustrated in the present case, as will be seen from the results and tests given. At any rate it may be safely said that silicon has been blamed in a somewhat hasty manner. This blame may be well deserved in alloys of carbon, silicon, and iron, as such alloys as regards ductility have, no doubt, proved unreliable and of little value; but the blame was put at the door of silicon, whereas it is now proved that silicon alloyed with iron, provided carbon is absent, or only present in small amounts, gives good tests as to toughness and malleability. It will be seen that 1½ or even 2 per cent may be present and yet the material possess 25 to 30 per cent elongation; whereas the same percentage of carbon alloyed with iron would give a product barely malleable, and one possessing practically no properties of elongation under tensile stress. Whilst, therefore, the common belief that alloys of carbon, silicon, and iron are brittle, or even dangerous, is quite correct, the cause is not due to silicon only, but to the combination of silicon with carbon and iron—a case parallel, to some extent, to that pointed out by the well-known Terre Noire Company's experiments, where it was proved that phosphorus may be present in iron provided the carbon is low and the manganese high; a fact—that is, as regards phosphorus—still more prominent in wrought irons. As also pointed out by Mr. Howe, "Silica is often mistaken for silicon: who knows how far it is responsible for this metalloid's bad name?" This was actually noticed by Mr. Turner in test bars of steel containing comparatively low percentages of silicon—that is, under 0·5 per cent—much of the silicon present being in the oxidised condition.

Also, according to M. Gautier, there is a difference between steel made with silicon only and that with silicon and manganese, *i.e.*, between a product made by adding ferro-silicon (carbon, silicon, and iron alloy) and that with silicon-spiegel (carbon, silicon, manganese, and iron alloy); and he mentions the following interesting experiment by his then colleague, M. Pourcel.

In a porcelain tube were placed two receptacles, one holding steel made by adding ferro silicon only, and the other steel by an alloy of silicon-spiegel. A current of chlorine was passed until all the iron was removed in the state of chloride. It was then seen that in the first receptacle there remained a network of silicate of iron preserving the original formation of the piece, whilst steel

* Third Report of the Committee, consisting of Professors Tilden and W. Chandler Roberts-Austen and Mr. T. Turner (Secretary), appointed for the purpose of investigating the Influence of Silicon on the Properties of Steel. Read before the British Association, Section B, Newcastle Meeting.

by silicon and manganese alloy left no residuum. Also, that such steel with no manganese was red-short, lacked fluidity, and possessed other defects. The writer has, however, not noticed such difference in the material now described, which in its molten state pours well, the ingots forging easily, and up to two per cent silicon the ductility in the testing-machine being very good.

However, as suggested by Mr. Howe, possibly silicon does enter into different combinations in steel, some promoting, some impairing ductility and malleability. In favour of this is the fact that so many well-known scientists and metallurgists have utterly condemned in forged steel the employment of silicon, even if present in small amounts. Such strong opinions would not be expressed without good grounds, and a reasonable explanation for the apparent discrepancy noticed by different observers seems to some extent to be in the direction named. At any rate the samples described in this paper, and containing up to two per cent, present a remarkable ductility and toughness both in the bending and tensile specimens.

The writer wishes it to be understood that he does not claim that silicon should take the place of carbon. Smaller quantities of carbon produce the requisite hardness and different tempers required in the industrial application of steel, and in fact silicon alone does not produce a steel that will harden by water-quenching, thus in this respect resembling manganese steel. Still it is a somewhat remarkable fact that a steel (specimen C) containing 1·60 per cent of a metalloid ordinarily so much distrusted stretched 35·10 per cent (on 2″), with 54·52 per cent reduction in area, and a test bar from the same material tested by Professor Kennedy gave 24·30 per cent (on 10″), with 58·30 per cent reduction in area. Also, had not the specimen D, tested by Professor Kennedy, broken in the threads (the diameter of the bar over the threads being only 0·93 against 0·898 of the tested part of the bar: too small a difference with hard steel in the holding part) no doubt his test would have confirmed the writer's, that a material with even 2·13 per cent of silicon will elongate 36·50 per cent on 2″ (equivalent to about 27 per cent on 10″), with 59·96 per cent reduction in area. So that whilst it may not be advisable to use silicon as a hardener in making steel, it is important to have it proved that the brittleness noticed in ordinary so-called silicon steel is due rather to the combined presence of the two hardeners, silicon and carbon. It may be here mentioned that the ductility noticed cannot be attributed to manganese, which was only present in small quantities, about 0·20 to 0·30 per cent.

The material employed in these experiments was made by melting in crucibles good wrought-iron scrap, low in sulphur and phosphorus, to which was added in varying and increasing quantities a rich ferro-silicon containing 20 per cent of silicon. The ingots, 2½ inches square, were reduced by forging in the ordinary method to 1¾-inch square billets, then rolled down to bars 1¼-inch diameter.

The effect of silicon upon iron is as follows; (1) in its forged condition; (2) in its cast condition:—

1. *Forged Condition.*—The forge reports that the material A (0·24 per cent Si) did not forge well, cracking somewhat whilst being hammered, but all the other samples, B to H (0·79 per cent to 5·53 per cent Si), when forged at a fair yellow heat required no special care; thus clearly showing that silicon even up to as high as about 6 per cent does not destroy the malleability of the metal iron. Upon, however, exceeding this percentage the material is red-short, crumbles at a low heat, and, notwithstanding the low percentage of carbon present (0·25 per cent), becomes really a species of cast-iron. It should also be here mentioned that if the carbon had been higher the point at which malleability ceases would have been with a much lower percentage of silicon.

Nor is such red-shortness removed by the addition of manganese.

It may also be here mentioned that no return of strength takes place by a further addition of silicon, as is so specially characteristic of manganese steel. Any further addition merely increases its resemblance to siliceous cast-iron. Nor do gradually increasing percentages, as is the case with manganese steel, destroy the magnetic properties of the alloy; a 7 per cent material seems quite as susceptible as ordinary iron drillings.

Apparently silicon up to 1⅛ or 1¼ per cent added to iron, although increasing the limit of elasticity and raising the tensile strength, does not impair ductility, but after this the further increase of tensile strength noticed is only obtained with a serious loss of ductility. Apparently there is no sharp line of demarcation. After passing 1½ per cent further slight increases cause great changes in the characteristics of the material. In this respect, therefore, its action rather resembles that of carbon in contradistinction to the action of manganese, of which much larger amounts are required to effect similar changes.

The fractures from the tensile test-bars up to "D" specimen (2·18 per cent Si) are silky, after this completely and coarsely crystalline. As in the specimens in the cast state, neither annealing nor water-quenching seem to have any effect on the structure.

The annealed flat bending pieces, ½ inch wide by ¼ inch thick, gave good results, specimens A, B, C, and D (0·24 per cent to 2·18 per cent Si) bending double cold without fracture, more like dead soft steel, and, after being bent double, the pieces were flattened close together cold without showing signs of fracture. Specimen E (2·67 per cent Si) also bent double cold, but broke in the radius with the least blow. F (3·46 per cent Si) was much stiffer, and bent only to a right angle. G and H (4·49 per cent and 5·53 per cent) would not bend at all, and were exceedingly brittle. These bending tests were confirmed by Mr. Turner's experiments with bars of the same size; up to D specimen the samples bent to an angle of 180° with ⅛ inch radius.

Pieces from the bars used for bending tests were also tested for weldability, but entirely without success. The writer's experience has always been that silicon is quite fatal to welding, notwithstanding that the contrary might be expected from the fact that silica is of such material assistance in welding wrought-iron.

As regards water-quenching or hardening, samples A, B, C, and D (0·24 per cent to 2·18 per cent Si) were unaffected by even the highest heat. Even if plunged at welding-heat into water made specially cold no hardening beyond a surface stiffening took place, nor did their toughness seem impaired by this treatment. Specimen E (2·67 per cent Si) was heated to an ordinary yellow heat and plunged into cold water at about 70° F. This piece was much stiffened, but only broke on being bent double. Another piece of the same material, heated to a welding heat and plunged into water at about 52°, also proved very stiff, and only broke when bent double; F (3·46 per cent Si): this sample was only stiffened by being water-quenched at a welding heat. It was just as brittle as before, and had not hardened, being easily touched by a file. In this respect, therefore, *i.e.*, as to being toughened by water-quenching, this material differs from manganese steel. The heating did not cause much alteration in fracture, the crystallisation being still open and coarse. H (5·53 per cent) was quenched both at ordinary heat and at a welding-heat, and although the surface was skin-hardened, upon being fractured it was easily filed. These tests, therefore, clearly prove that silicon does not confer the same property as carbon does upon iron, *i.e.*, of becoming hardened when dipped hot into a cooling medium. It should also be here stated that the whole of the samples were subjected to high heats, even to a welding temperature, without falling to pieces; in fact, as regards this point, they behaved more like mild steel; apparently proving that silicon itself does not cause iron to become red-short.

That silicon steel has a certain kind or degree of softness or lack of body compared with carbon-steel is especially brought out in the compression tests, where sample E, although apparently very hard and brittle (high in the scale of Turner's hardness tests, viz., 33), crushed up 38 per cent of its length under a compression load of 100 tons per square inch. A correspondingly hard temper of carbon or tungsten steel would not shorten more than 20 per cent, or, if hardened, would remain unaltered. A very mild steel, containing not more than 0·20 per cent of carbon, would not shorten much more than this sample, containing over 2½ per cent of silicon. At any rate, therefore, silicon is not so powerful a hardener of iron as is carbon. Mr. T. Turner has tested this material in his sclerometer, or hardness-testing machine, the results of which are given under this head in Table I.

In order to test this steel in the shape of wire, samples E (2·67 per cent Si) and G (4·49 per cent Si) were reduced to rods, and Messrs. Shipman and Co., of Sheffield, kindly undertook to draw them into wire. The G material, though readily rolled into rods, would not, however, draw, nor did annealing soften or give it the requisite ductility. In the rod state the tensile strength was 19 tons per square inch, with 12 torsions in 8 inches. Crucible carbon steel would stand about the same test, and Swedish Bessemer with high carbon slightly higher in torsion, but lower in tensile strength.

The material, E, was readily drawn to No. 20 B.W.G., standing 180 lbs. tensile strength (64 tons per square inch), with 157 torsions in 8 inches. Annealing lowered the tensile strength to 120 lbs. (about 48 tons per square inch), and slightly increased the torsions to 169 in 8 inches. The wire-makers endeavoured to harden both G rods and E wire both in oil and water, but without success.

Professor Barrett, F.R.S., of Dublin, has kindly undertaken to determine the electrical properties of the steel wire just mentioned, but the results are not yet completed. About twelve months ago the writer, thinking that silicon might confer upon iron qualities suitable for the manufacture of magnets, sent to Mr. Bottomley, in Sir W. Thomson's laboratory, Glasgow, a forged sample, containing 4·43 per cent of silicon and 0·18 per cent of carbon

(To be continued).

PREPARATION AND PROPERTIES OF ANHYDROUS PLATINUM BIFLUORIDE.

By H. MOISSAN.

In the researches undertaken hitherto for the isolation of fluorine, several *savants* have vainly sought to prepare platinum fluoride in the anhydrous state. It seemed according to the analogies of the fluorides and the chlorides, that platinum fluoride might be split up into platinum and fluorine by a mere rise of temperature. In 1856 M. Fremy wrote as follows :—"As for the gold and platinum fluorides, which would probably have given fluorine by ignition if I could have obtained them in an anhydrous state, it has been impossible for me to produce them by combining hydrofluoric acid with the hydrated oxides of gold and platinum."

That which was impossible—and we shall see below wherefore—on setting out from hydrofluoric acid and the hydrated oxides has become relatively easy on making use of platinum and fluorine. We have already had occasion, in our first researches on fluorine, to indicate that platinum is easily attacked by this body with the aid of heat.

We first determined at what temperatures platinum is attacked. When fluorine is really free from hydrofluoric acid, platinum in wire or foil is not attacked at 100°. For a decided formation of the compound a temperature of 500° to 600° is necessary. If platinum is immersed in a gaseous mixture of fluorine and hydrofluoric acid it is attacked more readily. It is the same when platinum remains in contact with liquid hydrofluoric acid saturated with fluorine, as in our electrolytic apparatus, in which case the platinum rod which serves as a positive electrode is rapidly corroded, even at a temperature bordering upon 0°.

As pure fluorine strongly attacks platinum at temperatures of 500° to 600°, in order to cause these bodies to combine it is merely requisite to heat to dull redness platinum kept in a current of fluorine gas. If the management of fluorine at common temperatures presents difficulties, it will be understood that the experiment requires some preparations. We take a bundle of platinum wires, which are introduced into a thick tube of platinum or into a tube of fluor-spar traversed by a rapid current of fluorine, and kept at dull redness. As soon as platinum fluoride is formed, the bunch of platinum wires is withdrawn from the apparatus and placed in a very dry glass tube. If the operation has been conducted in a platinum tube a considerable quantity of fluoride remains melted in the apparatus.

Platinum fluoride appears in melted masses of a deep red, or in small yellowish crystals resembling those of anhydrous platinum chloride in colour. It is very hygroscopic, and it cannot be preserved for some months without change, even in stoppered glass tubes which have been previously well dried. Its most curious reaction is that with water. If the fluoride is placed in a little distilled water in a platinum capsule there is at once produced a solution of a tawny colour, but almost immediately the liquid becomes heated the fluoride is decomposed, yielding hydrated platinic oxide and hydrofluoric acid. If the quantity of water is relatively large in proportion to the fluoride, and its temperature is low, the solution may be kept for a few moments without decomposition. As soon as the liquid is raised to a boil the above-mentioned decomposition is rapidly determined. This decomposition explains why it has hitherto been impossible to prepare the anhydrous platinum fluoride in the wet way. This compound cannot be produced in contact with water, as it rapidly decomposes that liquid, the fluorine uniting with the hydrogen to form hydrofluoric acid, and the platinum combining with oxygen to form a yellowish brown precipitate, soluble in potassa, and approximating in its properties to the hydrated bioxide of M. Fremy, PtO_2H_2O.

At redness, platinum fluoride is split up into fluorine and metallic platinum. This experiment may be made by heating to redness the fluoride obtained as above in a platinum tube closed at one end. If crystalline silicon is then placed at the open end of the tube the silicon takes fire at the common temperature, indicating distinctly the liberation of the fluorine. If the platinum resulting from this decomposition is examined it is found to be crystalline. This new instance may be added to those which occasioned M. Daubrée to call attention to the mineralising *rôle* of fluorine, which has since been confirmed by the fine mineralogical syntheses of H. Sainte-Claire Deville and M. Hautefeuille.

The analysis of platinum fluoride has been made by dissolving this salt in much cold water, decanting rapidly to remove the small quantity of insoluble platinous fluoride which is formed on contact with the metal. The liquid is then decomposed at the boiling-point. It is evaporated to dryness, ignited, and the composition of the fluoride soluble in water is deduced from the weight of the platinum. The analyses answer to the formula $PtFl_2$.

Gold, under the same conditions, yields a dark-coloured very hygroscopic fluoride, decomposable by heat into fluorine and metal.

In fine platinum difluoride $PtFl_2$ decomposes water at common temperatures. At a red heat it is resolved into crystalline platinum and fluorine. If this compound can be obtained by an indirect manner, which may possibly

be effected, it will be easy to have a preparation of fluorine based upon a purely chemical reaction.

As pure fluorine has no action upon platinum at common temperatures, it becomes possible to determine its physical constants. M. Moissan hopes soon to submit to the Academy new researches on the density, the colour, and the spectrum of fluorine.—*Comptes Rendus* (Vol. cix., p. 807).

ON THE REDUCTION OF ALUMINIUM.*

By Dr. WAHL

At the meeting on October 15th Dr. Wahl made some remarks on the industrial production of aluminium by electrolysis. He referred to the process of M. Adolphe Minet, in operation industrially at Creil (Oise), France, and which, in essential parts, was identical with that of Mr. Hall. Mr. Minet electrolyses a bath composed of forty per cent of cryolite and sixty per cent of chloride of sodium, maintained in the state of igneous fusion. The bath is continually regenerated by additions of alumina (or bauxite). The interesting point in considering the two processes, the speaker stated, was the different explanations of the operations taking place in the bath under the action of the electric current upon substantially the same components; Hall claiming that the alumina undergoes electrolysis, the solvent fluorides being unaffected, and Minet that the fluorides are electrolysed, the liberated fluorine acting upon the alumina, to form fresh fluoride, thus maintaining the bath. The explanation of M. Minet, the speaker held, to be the rational one.

NOTICES OF BOOKS.

Iron and Steel Manufacture. A Text-Book for Beginners. By Arthur H. Hiorns, Principal, School of Metallurgy, Birmingham and Midland Institute. London: Macmillan and Co.

This little work is to some extent intended for examinational purposes, since, in the preface, we are informed that "Pupils preparing for the ordinary grade examinations of the City and Guilds of London Institute will find the questions at the end of each chapter specially useful." Whether they have been selected from papers set on occasion of former examinations we are unable to say. The subjects taken up are treated briefly, of course, seeing that the entire work extends only to 180 pages, including the index, but clearly and correctly.

Very few passages require notice. It does not appear what is the exact nature of the "Belfast aluminous ore," described here as similar to bauxite. It quite disagrees in composition, according to the analysis given, with the "Eglinton alum clay" from the North-east of Ireland, which contains more alumina, more combined water, and very much less ferric oxide.

The residual matter from roasting iron-pyrites in the manufacture of sulphuric acid is here spoken of as "blue billy." In the Lancashire alkali district it is ordinarily named "burnt ore," whilst the name "blue billy" is commonly given to the spent lime from the gas-purifiers.

The masses of meteoric iron mentioned on p. 28 cannot be considered as the largest on record.

The illustrations, eighty in number, are well selected, and add much to the value of the book.

An Introduction to Chemical Science. By R. P. Williams, A.M. Edited and revised by B. P. Lascelles, M.A., F.C.S. London: Ginn and Co.

This is an ably written treatise, and may be recommended if, indeed, there is necessity or even room for any more elementary works on chemistry. It has the merit of making no reference to any code, syllabus, or examination. Its greatest deficiency is, in our opinion, the omission of the Periodic Law, which now forms so essential a feature in chemical theory. In the table of the principal elements we note that the author and editor still retain the old atomic weight for platinum, making it higher than that of gold.

A few other errors have escaped notice. Thus, we read that "Graphite is found in the oldest rock-formations in the United States and Siberia." Now, though graphite certainly occurs in the United States, to us in Britain the deposits of that mineral in Ceylon and in Bavaria are of greater importance.

In § 73 we note an un-English expression; the pupil is told to "touch a drop *to* the tongue, noting the taste." A correct writer would have said "*with* the tongue." Sulphuric acid, we read, is used in making "indigo and madder." Perhaps the author means the so-called extract of indigo.

It is stated that fashionable women sometimes eat arsenious acid "for the purpose of beautifying the complexion, to which it imparts a ghastly white unearthly hue." We fear that this evil habit is gaining ground both in America and on the European Continent. How anyone can think a ghastly complexion beautiful we fail to see. The injurious effects of arsenical wall-papers here mentioned as doubtful have unfortunately become past all doubt, though the idiosyncrasy of persons exposed to their influence plays here a great part.

Under alcohol it is mentioned that the American courts now regard all liquors having three per cent or less of alcohol as not intoxicating. In Massachusetts it (the limit) is one per cent. If such were the rule in Britain, most of the "temperance" beverages sold would come under the jurisdiction of the excise.

The Clinical Use of Prisms and the Decentering of Lenses. By Ernest E. Maddox, M.B. Bristol: Wright and Co. London: Hamilton, Adams, and Co.

This work cannot well be considered to fall within our cognisance, as its merits can only be estimated by the practical ophthalmic surgeon. The author discusses in the first place prisms from the geometrical, the optical, and the clinical point of view. He then passes on to "marking the apex," prismetry, planeness of surface, adjustment in trial frame, and temporary trials. He then takes up the decentering of lenses, localisation, the analysis of spectacles, and the chief clinical applications of prisms, viz., in the consulting-room and in spectacles.

The Geological Record for 1880—1884 (inclusive): A List of Publications on Geology, Mineralogy, and Palæontology Published during those years; together with certain References Omitted from Previous Volumes. Edited by W. Topley, F.R.S., F.G.S., and C. D. Sherborn, F.G.S. Vol. II., Physical and Applied Geology, Petrology, Meteorites, Mineralogy, Mineral Waters, Palæontology, General, Maps, and Sections. London: Taylor and Francis.

This volume will be of the greatest value to geologists, especially if desirous of knowing what has been done in any particular department of their science, but as it contains no abstracts of the memoirs indexed it cannot be reviewed.

Annual Report of the Board of Regents of the Smithsonian Institution: Showing the Operations, Expenditure, and Conditions of the Institution for the Year ending June 30th, 1886. Part I. Washington: Government Printing Office, 1889.

Whilst this Report gives proof of abundant and valuable work in other departments of science, chemistry has

* From the Chemical Section of the *Journal of the Franklin Institute*, Nov., 1889

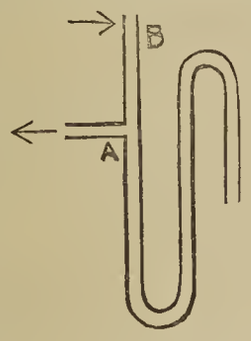
not fared nearly so well as, *e.g.*, ethnology. We find here no chemical matter, except a brief notice of the researches on the venom of serpents, by Messrs. Mitchell and Reichert: no details are given.

CORRESPONDENCE.

WATER-BATH REGULATOR.

To the Editor of the Chemical News.

Sir,—In the last issue of the *Chemiker Zeitung* an abstract appears of an article from your valued journal describing Mr. Easterfield's water-bath regulator. It may possibly interest you to know that I recently devised an arrangement for the same purpose very similar to the above; but, I think, more easily extemporised. Mine is of lead pipe, with an ordinary brass T-piece at A.



Water enters from a small elbow tube loosely resting on B, but without closing the latter. The exit is at A, which must be at the water-level to be maintained in the bath; this level may be easily altered, when desired, by bending the pipe.—I am, &c.,

Charles E. Sohn, F.C.S., A.I.C.

25, Beverley Road, Anerley, Surrey,
December 9, 1889.

STANDARD SOLUTION OF FERRIC SALTS WITHOUT TITRATION.

To the Editor of the Chemical News.

Sir,—The use of ferrous ammonium sulphate in the production of standard iron solutions for titration is not new. Mr. French will find it in Sutton's "Volumetric Analysis," published as far back as 1863.—I am, &c.,

H. N. D.

Dublin.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 22, November 25, 1889.

Animal Heat. Heat developed by the Action of Oxygen upon the Blood.—M. Berthelot.—When Lavoisier recognised that animal heat is essentially a phenomenon of combustion, he raised the question whether this combustion takes place in the lungs themselves at the point where the oxygen is absorbed and the carbonic acid given off, or if it is produced in the entire system, the absorption of the oxygen taking case in virtue of a first reaction effected at the expense of the blood. M. Berthelot now finds that the animal heat may be resolved into two portions; one part, about the seventh, is produced in the lungs themselves by the fixation of oxygen, whilst the remaining six-sevenths are developed in the system by reactions of oxidation and hydration. The absorption of oxygen tends to raise the temperature of the blood in the lungs, whilst the return of the carbonic acid to the gaseous state and that of watery vapour tend to lower it.

Exhaustion of Soils by Cultivation without Manures, and the Utility of the Organic Matter of the Soil.—P. P. Dehérain.—The author is led to admit that the organic matter of the soil serves directly as a plant-food. He compared experimentally the vegetation of sugar-beets in a soil rich in organic matter and in a soil poor in humus, but watered and mixed with nitrates, phosphates, and salts of potassium. He took two large earthenware pots, varnished externally, and capable of holding 30 kilos. of soil, and filled them, the one with a soil rich in humus, the other with an exhausted soil. The poor soil was watered and received the addition of 3 grms. sodium nitrate, 3 grms. of calcium superphosphate, and the same weight of potassium chloride. A single beet was allowed to remain in each. The beet which had grown in the rich soil weighed 730 grms.; the root alone, 410; the sugar in 100 parts of the juice, 15·04; and the total sugar, 61·60 grms. The plant grown in the poor soil which had received the mineral manures weighed only 165 grms.; the root alone, 92; the percentage of sugar was 11·11; and the entire weight of sugar, 10·12 grms. The simplest interpretation of the facts seems to be that the organic matter forms a necessary part of the food of the plant, just as do the nitrates, the phosphates, and the potash, and that its absence is as prejudicial as that of any of these mineral constituents.

Preparation and Properties of Anhydrous Platinum Fluoride.—H. Moissan.—This paper will be inserted in full.

A Contribution to the Study of Double Decompositions between the Haloid Salts of Mercury and of Zinc.—Raoul Varet.—The action of mercury cyanide upon zinc bromide and that of zinc cyanide upon mercury lead to the system ($HgCy.HgBr.ZnCy + HgB$). The production of the triple salt $HgCy.HgBr.ZnCy + 8HO$ leads to an equilibrium which limits the inverse reactions which might reproduce one of the original systems, whether $Hg_2Cy_2 + Zn_2Br_2$, or, on the contrary,—

$$Hg_2Br_2 + Zn_2Cy.$$

All the zinc cyanide does not take part in the formation of the triple salt, and the quantity which enters into combination depends both on the proportion of water and the proportion of mercury cyanide dissolved therein.

A New Sugar with an Aromatic Nucleus.—M. Maquenne.—The two pinites, and probably also sennite, are closely connected with the aromatic series, and form ethers derived from a new principle, isomeric with the glucoses, and which appears to answer to the same formula as inosite.

Synthesis of Metaphenylene Diamine from Resorcine and Ammonia.—Alphonse Seyewitz.—Below 150° resorcine and ammonia do not react; the amine is only formed at upwards of 200°, the yield of diamine increasing with the temperature. Below 250° resorcine remains always unattacked.

Action of Heat upon Chloralammonium.—A. Béhal and M. Choay.—This paper does not admit of useful abstraction.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. vi., No. 2.

Determination of Sulphur in Burnt Pyrites.—The process of Watson is mentioned as simple, practical, and fairly accurate. The directions given are to mix 2 or 3 grms. of the ore finely ground with 1 or 2 grms. of sodium

hydrocarbonate of known alkalimetric value, and heat the mixture for five to ten minutes in a crucible of porcelain, nickel, or platinum. The mixture is then stirred up and heated again more strongly for fifteen minutes. Lastly, the mass is extracted with boiling water, filtered, and the excess of alkali determined volumetrically by means of normal hydrochloric acid, using methyl-orange as indicator.

MISCELLANEOUS.

An Appeal.—Mr. G. F. Rodwell, after twelve years of good service at Marlborough College, was struck with paralysis and aphasia in 1883, and has since then been utterly incapacitated for work of any kind. He had, for a long period, helped to support an invalid mother and sister, and his seizure is attributed in part to extra work undertaken, both in term and vacation, for this object. In the hope of recovering his general health and nervous power, Mr. Rodwell has undertaken voyages to America and elsewhere, which have utterly failed to restore him, but have exhausted the larger part of his savings; so that he is now left with a bare £300 of capital, and no other source of income, while he has no kinsfolk able to maintain him. The Council of the College made him a grant of 200 guineas in 1883, and have recently voted him £50, with an intimation that they will again consider his application at the end of twelve months. He had long cherished a hope that in consideration of his scientific and literary labours a pension might be awarded to him from the Civil List; and every effort was made to recommend him for such a pension; but the hope of it has now been finally abandoned. Under these painful and exceptional circumstances it is thought that many of Mr. Rodwell's old friends and pupils will be ready to show their sympathy for him by contributing to a fund for the purchase of a small annuity on his life. Contributions may be sent to The Master, The Bursar, or M. H. Gould, Esq., Marlborough College, or to his sister, Miss Rodwell, Parkbrook, Hampton-on-Thames.

Royal Institution.—The following are the Lecture Arrangements before Easter:—

Professor A. W. Rücker, Six Christmas Lectures to Juveniles, on "Electricity."

Professor G. J. Romanes, Ten Lectures on "The Post-Darwinian Period."

Mr. E. Roscoe Mullins, Three Lectures on "Sculpture in relation to the Age."

The Rev. Canon Ainger, Three Lectures on "The Three Stages of Shakspeare's Art."

Mr. Frederick Niecks, Four Lectures on "The Early Developments of the Forms of Instrumental Music" (with Musical Illustrations).

Professor Flower, Three Lectures on "The Natural History of the Horse and of its Extinct and Existing Allies."

The Right Hon. Lord Rayleigh, Seven Lectures on "Electricity and Magnetism."

The following are the arrangements for the Friday Evening Meetings:—

Jan. 24th. Professor Dewar, M.A., F.R.S.—"Scientific Work of Joule."

Jan. 31st. Sir Frederick Abel, C.B., D.C.L., D.Sc.—"On Smokeless Explosives."

Feb. 7th. Henry B. Wheatley.—"The London Stage in Elizabeth's Reign."

Feb. 14th. Professor J. A. Fleming.—"Problems in the Physics of an Electric Lamp."

Feb. 21st. Shelford Bidwell.—"Magnetic Phenomena."

Feb. 28th. Professor C. Hubert H. Parry.—"Evolution in Music."

March 7th. Francis Gotch.—"Electrical Relations of the Brain and Spinal Cord."

March 14th. Professor T. E. Thorpe.—"The Glow of Phosphorus."

March 21st. Professor G. F. Fitzgerald.—"Electromagnetic Radiation."

March 28th.—The Right Hon Lord Rayleigh.

NOTES AND QUERIES.

*** Our Notes and Queries column was opened for the purpose of giving and obtaining information likely to be of use to our readers generally. We cannot undertake to let this column be the means of transmitting merely private information, or such trade notices as should legitimately come in the advertising columns.

Nickel and Cobalt.—Would you inform me through your correspondence in the Chemical News which is the best standard metallurgical work on nickel and cobalt?—Nickel.

MEETINGS FOR THE WEEK.

Monday, Dec. 16th.—Medical, 8 30.
—— Society of Arts, 8. (Cantor Lectures). "Modern Developments of Bread-making," by William Jago.
Tuesday, 17th.—Institute of Civil Engineers, 8.
—— Pathological, 8.30
Wednesday, 18th.—Society of Arts, 8. "London Sewage," by Sir Robert Rawlinson, K.C.B.
—— Meteorological, 7.
—— Geological, 8.
Thursday, 19th.—Royal, 4 30.
—— Royal Society Club, 6.30.
—— Chemical, 8. "On Frangulin," by Prof. Thorpe, F.R.S., and H. H. Robinson, M.A.

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FOR SALE.—The Chemical Gazette. Complete Set (unbound and uncut), 17 volumes; from November, 1842, to December, 1859.—Address, "Publisher," Chemical News Office, Boy Court, Ludgate Hill London, E.C.

THE CHEMICAL NEWS.

Vol. LX. No. 1569.

SOME PENDULUM EXPERIMENTS IN RELATION TO THE MUTUAL APPROACH OF THE BODIES, AND A SUGGESTION AS TO THE CAUSE OF THAT APPROACH.

By J. BAYNES THOMPSON.

Mutual attraction is said to cause that approach, but I can find no one who can conceive a possible mode of the action of attraction; how one piece of crude matter can reach across space and pull another piece of matter towards itself. Absurd as that appears, it is just what attraction means if it has any meaning at all. No one has ever proved by experiment or by reason from experiment that there is such a thing as attraction. All that experiment has proved to our senses is that bodies do tend to approach. The how is a deduction of reason which has not been made.

The general opinion of physicists may be obtained from "Ganot's Physics." It is that universal attraction is a force in virtue of which the material particles of all bodies tend incessantly to approach each other. *The nature of the force is entirely unknown.* We are at a loss whether to consider it as a general property inherent in matter, or whether the effects of which it is the cause are due to the action of some external agent. *It is a mutual action, however, which all bodies at rest or in motion exert upon one another*, no matter how great or how small the space between them may be, or whether the space be occupied or unoccupied by other matter. . . . . "The attraction between any two bodies is the resultant of the attraction of each molecule of the one upon every molecule of the other according to the law of Newton, which may be thus expressed.

"*The attraction between two material particles is directly proportional to the product of their masses, and inversely proportional to the squares of their distances asunder.*

"To illustrate this we may take the case of two spheres which, owing to their symmetry, attract each other just as if their masses were concentrated in their centres. If, without other alteration, the mass of one sphere were doubled, trebled, &c, &c., the force will be doubled, trebled, &c. If, however, the mass of one sphere being doubled, that of the other were increased three times, the distance between their centres remaining the same, the attraction would be increased six times."

This statement is rather contradictory. It begins with the statement that the nature of the force of attraction is "*entirely unknown*"; but further on it states that it is a mutual action, however; so that, according to that, the nature of it is not entirely unknown. Further, it states:—"We are at a loss whether to consider it a universal property inherent in matter, or whether the effects of which it is the cause are due to the action of some external agent." That is not very clear, but it appears to mean that it is not known whether the cause is mutual attraction or external pressure. Yet, immediately after, it is stated that each particle of matter attracts every other particle of matter, each directly according to its mass, and gives examples as illustrations, just as if everything was known about it.

The latest statement on this matter is by Professor Young in his "Text-book of General Astronomy" published this year (1889) in Boston, U.S.A. Under the heading "Gravity" he says:—"The law of gravitation discovered by Newton declares that any particle of matter attracts any other particle with a force (stress if the bodies are prevented from moving) proportional to the inverse squares of the distance between them, and directly to the product of their masses; or, as a formula, may be written—

$$\mathrm{FK}\,\frac{m_1 \times m_2}{d_2}.$$

m_1 and m_2 are the masses, d the distance, F the force, and K a constant numerical factor depending on the units employed. He then makes the following remarks:—

"We must not imagine the word 'attract' to mean too much. It merely states the fact that there is a *tendency* for the bodies to move towards each other, without including or implying any explanation of the fact. So far no explanation has appeared which is less difficult to comprehend than the fact itself. Whether bodies are *drawn together* by some outside action or pushed together; or whether *they themselves can act across space with mathematical intelligence*—in what way it is that 'attraction' comes about is still unknown. Apparently as inscrutable as the very nature and constitution of an atom of matter itself. *It is simply a fundamental fact.*"

Evidently Professor Young did not well consider these remarks before he put them down. He begins by saying that attraction does not mean attraction at all, when he has just written down the law of mutual attraction and given a formula by which to calculate the force of attraction. Then he says we do not know whether bodies are drawn together by some outside action, but an outside action or force could act only by pushing. The next suggestion is unique as an attempt to explain mutual attraction. He says we do not know whether matter may not be able to act across space with mathematical intelligence!

Just think! Metals, stones, and brickbats may have mathematical intelligence! Of course that only means that Professor Young cannot comprehend mutual attraction any more than anyone else. Still, as a final remark he says:—"*It is simply a fundamental fact.*" Now, how can Professor Young know that it is a fundamental fact, or even a fact at all? since he confessedly comprehends nothing about it. Clearly no assistance can be derived from the opinions of scientists on this matter. The only resource remaining is experiment, to see if any light can be obtained from the facts.

For the purpose of these experiments I have imagined several modifications of Cavendish's apparatus; but the manipulation was so difficult, and it was not easy to get the weight corresponding with the torsion; moreover, the torsion was not constant in any wire that I used. Therefore I devised a pendulum apparatus, and had it made. It is very steady and easy to manipulate; moreover, with it the force acts against gravity; consequently it is easy to calculate. For example, take the pendulum at the perpendicular; gravity is then annulled by the support of the pendulum rod. Now raise the pendulum through 90°, and the full force of the weight of the bob and half the weight of the rod will be exerted, and at every angle from that to the perpendicular the weight will be proportional to the vers-sine of the angle of divergence from the perpendicular, and the vers-sine is easily found.

Take the pendulum as radius r, angle of divergence

Then r − co-sine = vers-sine.

Now let weight of bob, &c., be Wt, and force causing the deviation F, and the force is found as follows:—

$$r : \text{vers-sine} :: \mathrm{Wt} : \mathrm{F} = \frac{\text{vers-sine} \times \mathrm{Wt}}{r} = \mathrm{F}.$$

The actual apparatus has the following parts and dimensions. The pendulum is 42 inches long; it works on a steel knife-edge, and has a needle at the bottom as pointer. Below this there is a micrometer. The screw of this micrometer has twenty threads to the inch. It works in a bearing at one end, having a collar to keep it

in its place; at the other it moves on a pivot which has a set screw to keep it in its place when screwed up, so that the micrometer screw may not shake. On the micrometer screw there is a block with a needle fixed in it, which can be placed under the pendulum needle, point to point. The shaft of the screw passes through the side of the case and through a dial placed outside. This dial has upon it a circle of 5 inches circumference. Each inch is divided into 10 parts. At the end of the screw-shaft is fixed a head with a needle in it as pointer, so that when this pointer moves over $\frac{1}{10}$ inch, the needle in the block on the screw moves over one-thousandth of an inch. It would be easy to measure 1-2000th of an inch by moving the pointer over half a tenth, but that length could scarcely be perceived at the micrometer needle. As pendulum bobs I have cylinders of lead, one $2\frac{1}{2}$ in. diameter and $2\frac{1}{2}$ in. long, the other $2\frac{1}{2}$ in. diameter and 5 inches long. They have $\frac{5}{10}$ in. holes through them, both longitudinally and transversely, so that they can be mounted vertically and horizontally; their weights are 5 lbs. and 10 lbs. The pendulum rod weighs $8\frac{1}{2}$ ozs., but the bob-half of the rod weighs 4 ozs. and the head-end $4\frac{1}{2}$ ozs. on account of the steel head and only a needle at the other end. The pendulum rod is a light brass tube. Besides the two cylinders mentioned there are two other similar cylinders to place stationary opposite the bob; they are also 5 lbs. and 10 lbs. weight and $2\frac{1}{2}$ in. diameter, $2\frac{1}{2}$ in. and 5 in. long. The case stands on levelling screws.

The mode of using the apparatus is as follows, it having been first levelled:—

The pendulum is steadied and allowed to come to rest; then the micrometer screw is turned till the point of the needle comes opposite the point of the pendulum needle, and the place of the pointer on the dial is noted. The required cylinder is placed opposite the bob of the pendulum at $\frac{1}{32}$ in. from it. The cylinder is placed vertical if the bob be vertical, and horizontal if the bob be horizontal. The pendulum will be found to have moved towards the fixed cylinder. When it has come to rest the micrometer screw is turned till the point of the needle is again opposite the point of the pendulum needle and the position of the pointer on the dial is noted. The difference between the two positions of the pointer on the dial shows the length of arc the pendulum has passed over, and this gives the angle of deviation from the perpendicular.

The following table shows a series of eight experiments, which have been repeated many times with but little variation.

	Position.	Cylinder on pendulum.	Cylinder fixed.	Arc passed over in inches.	Angle of deviation.	Force in m.grms.
		Lbs.	Lbs.			
1.	Vertical ..	5	5	0·013	1′3″5	28·353
2.	,, ..	5	10	0·013	1′3″5	28·353
3.	Horizontal..	5	5	0·013	1′3″5	28·353
4.	,, ..	5	10	0·026	2′7″0	56 707
5.	Vertical ..	10	10	0·013	1′3″5	56·245
6.	,, ..	10	5	0·007	34″	28·670
7.	Horizontal..	10	10	0·013	1′3″5	53·245
8.	,, ..	10	5	0·007	34″	28·670

Now let us try to interpret these experiment, first as to the cause of approach being mutual attraction, and then as to what they point to as the real cause of approach. No. 1 is 5 lbs. and 5 lbs. vertical, the measured arc passed over by pendulum is 0·013 in. and calculated force 28·353 m.grms. No. 2 is 5 lbs. and 10 lbs. vertical, the arc passed over and calculated force the same as with the two 5 lb. cylinders; but this is a 5 lb., and a 10 lb., therefore, ought to be double if caused by mutual attraction.

Now take No. 4, the same two cylinders as No. 2, but placed horizontally—that is, end to end—the pendulum bob being 5 lbs. as before. The measured arc that the pendulum has passed over is just double and the calculated force just double. This cannot be caused by mutual attraction, as the masses are the same as before; but it is simply from position.

No. 5 is 10 lbs. and 10 lbs. Here the arc passed over is the same as that passed over with the 5 lbs. and 5 lbs., but the masses being nearly double, namely, $5\frac{1}{4}$ to $10\frac{1}{4}$ on the pendulum, the force is nearly double. But the products of their masses are nearly as one to four; therefore, if the law of mutual attraction were true, the force should be nearly four times.

No. 6, the fixed cylinder, is about half the preceding cylinder; the arc is 0·007 instead of 0·0065, but the dial showed 0·007. We put it back half-a-tenth, but, with the naked eye, could not discern the difference at the micrometer needle; therefore we left it at 0·007 by calculation; that of course showed a little more than half. No. 7, 10 lbs. and 10 lbs. end to end; they gave the same as when side by side. No. 8, 10 lbs. and 5 lbs.; this gave the same as No. 6, when the cylinders were side by side.

According to these experiments there is no such thing as mutual attraction; therefore bodies mutually approach each other if free to move, from some other cause. As that cause I would suggest the pressure of the ether. Two bodies being free to move and near enough to each other, they each screen the other from the opposite bombardment of the ether by so much as their molecules stop the streams of ether molecules from passing through them; and these experiments seem to point to that as the cause. In No. 1 the cylinders were equal. In No. 2 the fixed cylinder is double what it is in No. 1, but the approach and force are the same. They are side by side vertically and their centres are opposite; but the larger cylinder can screen the smaller only to the size of the smaller, the parts of the larger cylinder above and below the smaller having no effect on the smaller cylinder. No. 3, 5 lbs. to 5 lbs. end to end, screen each other as before, being $2\frac{1}{2}$ in. through each way. No. 4, 5 lbs. to 10 lbs. end to end. The force here is double that of $2\frac{1}{2}$ and $2\frac{1}{2}$, because the 5 in. cylinder screened the $2\frac{1}{2}$ inch double. The other four experiments show the same thing; viz., that in proportion as the fixed cylinder screens the movable one, so is the force that causes the movable one to approach the fixed one.

As to the inverse squares, I have made some experiments on that also. The following table shows them. I took the 5 lb. cylinder on the pendulum and the 10 lb. cylinder fixed, because they give the greatest angle of deviation:—

Inches apart.	Arc passed over. Inches.	Force in M.grms.
$\frac{1}{32}$	0·026	56·707
$\frac{1}{8}$	0·024	52·345
$\frac{1}{4}$	0·023	50·164
$\frac{1}{2}$	0·022	47·983
$\frac{3}{4}$	0·021	45·802
1	0·020	43·621
$1\frac{1}{4}$	0·019	41·440
$1\frac{1}{2}$	0·018	39·259
$1\frac{3}{4}$	0·017	37·078
2	0·016	34·897
$2\frac{1}{4}$	0·015	32·716
$2\frac{1}{2}$	0·014	30·535
$2\frac{3}{4}$	0·013	28·354
3	0·012	26·173
$3\frac{1}{4}$	0·011	23·992
$3\frac{1}{2}$	0·010	21·811

In this table there does not appear to be any ratio between the distance apart, the arc passed over, and the corresponding force. However, it is certainly not as the inverse squares of the distance asunder.

The Methods of Teaching Chemistry.—We are informed by the Secretary of the Committee appointed by the British Association to enquire into the methods at present adopted in teaching chemistry that their second Report, made at the recent Newcastle Meeting, has now been put on sale by the Council. It may be obtained from the office of the Association, 22, Albemarle Street, W.

OSMOTIC PRESSURE:

With Special Reference to the Work of Rüdorff and Raoult.*

By EMILY J. LLOYD.

(Concluded from p. 286).

In 1883, M. F. M. Raoult, Professor of Chemistry at Grenoble, took up the subject (see *Annales de Chimie et de Physique*, 1883, 1884, 1885, 1886).

He examined first the freezing-point of solutions of some thirty organic substances, representatives of the varlous groups, except hydrocarboons — monatomic and polyatomic alcohols, sugars, glucose, phenols, aldehyds, acids, ethers, amides, amines, &c. These bodies differ as much in solubility and molecular weight as in chemical properties. The *coefficients of depression* of the freezing-points range from 0·052 to 1·117 (proportion 1 : 21½) ; but the *molecular depression* approximates, in most cases, to somewhere about 19. Hence, Raoult concludes that :—

1. The molecules of different organic matters dissolved in the same quantity of water cause approximately the same depression in the freezing-point of the solvent.

2. The constitution of the body exerts a feeble though evident influence on the freezing-point. But the depression depends more on the nature of each atom than on the place it holds in the compound (for acids the constant approximates to 19, for sugars to 18, for alcohols to 17). From this Raoult calculates that there should be fixed coefficients for each element. He found these to be : for H 15, for C 15, for O 30, for N 30.

Then for any substance, $C_pH_qN_rO_s$, the molecular depression is—

$$\frac{15p+15q+30r+30s}{p+q+r+s}.$$

In cases where the vapour density of a compound cannot be determined, Raoult claims this method to be of great importance in determining the molecular weight ; he decides in favour of that number *which multiplied by the coefficient of depression approaches most nearly to* 19.

Thus, in the case of oxalic acid, the molecule must be one of the following :—

$$CHO_2=45,\ C_2H_2O_4=90,\ C_3H_3O_6=135,\ \&c.$$

The calculation for the molecular depression is—

$$\frac{15n+15n+2\times30n}{4n} = \frac{90}{4} = 22{\cdot}5.$$

Experiment gives for the coefficient of depression 0·255. Now, if M = the molecular weight,

$$M\times0{\cdot}255=22{\cdot}5,$$

whence—

$$M=88{\cdot}3;$$

i.e., among the above possible formulæ we choose the second, the molecular weight of which approaches most nearly to 88·3.

The calculated number does not always agree very closely with the observed. Raoult gives this explanation ; "The molecules of an organic compound seem simply separated by the act of solution. As vaporisation does not completely separate the molecules of a body, so, in all probability, neither does solution."

Raoult next (*Ann. de Ch. et de Phys.*, 1884) published the results of his investigations on other solvents.

1. *Acetic Acid.*— Of the fifty-nine substances, mostly organic, with which Raoult experimented, the molecular weights varied from 18 to 690. The coefficients of depression ranged between 0·062 and 1·830 ; but in fifty-six cases the product M A (where M = molecular weight, A = coefficient of depression) approximated to 38.

In the three other cases (sulphuric and hydrochloric acids and magnesium acetate) M A = very nearly 18.

2. *Formic Acid.*—Raoult made fewer experiments with this solvent, but he found that the coefficients of depression, as before, varied considerably, 0·067 to 0·593, while the product M A in every case but one (that of magnesium formate) approched the number 28; for magnesium formate it was 13·9.

3. *Benzene.*— In this case the maximum molecular depression for some forty-two substances is about 50. With the hydrocarbons and their derivatives, ethers, aldehyds, acetones, nonoxygenated acids, and metallic chlorides M A = 49. With alcohols, phenols, and acids containing the group OH, the molecular depression approaches a mean of 25, just half the other number, as noticed with acetic and formic acids as solvents.

4. *Nitrobenzene.*—The same law is seen to obtain in this case. For thirteen out of the eighteen substances dissolved M A is never higher than 73 6, and approaches the mean 71 ; this for hydrocarbons and their substitution derivatives, ethers, aldehyds, acetones, chlorides of the metalloids ; but, as with benzene for solvent, alcohols and acids containing the hydroxyl group, give a product, M A, rather more than half that in the other cases.

5. *Ethylene Di-bromide.*—

	A =	M A =
For CS_2	1·534	116·6
,, $CHCl_3$	0·991	118·4
,, C_6H_6	1·528	119·2
,, $(C_2H_5)_2O$.. ..	1·588	117·5
,, $AsCl_3$	0·650	118·1
,, $C_2H_4O_2$	0·961	57·7
,, C_2H_5OH	1·234	56·8

Raoult concludes his second paper with the following generalisations :—

1. Every body in solution, liquid or gaseous, lowers the freezing-point of its solvent.

2. There is for each solvent a maximum lowering.

3. Every solution has two constants, the one double the other.

4. Whatever be the nature of the mutual action of the solvents, it is approximately the same for all solvents.

This statement requires some explanation. To consider the action of one molecule of the dissolved substance on one molecule of the solvent we must divide the molecular depression by the molecular weight of the solvent. We then get the remarkably coincident numbers :—

For [water	$\frac{47}{18}$ = 2·61]
,, formic acid	$\frac{29}{46}$ = 0·63
,, acetic acid	$\frac{39}{60}$ = 0·65
,, benzene	$\frac{50}{78}$ = 0·64
,, nitrobenzene	$\frac{73}{125}$ = 0·59
,, ethylene di-bromide .	$\frac{119}{188}$ = 0·63

i.e., The action of the *solvent* is independent of its nature —a result which might be expected from the fact that the action of the dissolved substance depends, not on the nature or arrangement of the atoms which compose the molecule, but on the number of the molecules. Another way of stating this is :—

Lowering of the freezing-point of a solution =

$$0{\cdot}63\times\frac{\text{No. of molecules of substance}}{\text{,, ,, solvent}}.$$

Water gives the number 2·61 as a maximum. From various considerations, Raoult afterwards concluded that the water molecule is really double the steam molecule, H_2O.

The above statements refer to organic substances only. For inorganic substances the numbers found by Raoult varied between 34 and 46. He therefore undertook further researches on their solutions in water. The results were published in the *Ann. de Ch. et de Phys.* for 1885.

The first noticeable regularity is the relation between similar salts of monad and diad metals of monatomic and polyatomic radicles.

* A Paper read before the Mason College Chemical Society, October 16, 1889.

		Difference.			
Ba_2OH	49·7	$2KHO$	70·6	20·9
Ba_2ClO_3	44·1	$2KClO_3$	66·4	22·3
Ba_2NO_3	40·5	$2KNO_3$	61·6	21·1
$Ba_2PH_2O_2$.. ..	50·7	$2KPH_2O_2$	72·2	21·5
$Ba_2C_2H_3O_2$ ..	49·2	$2KC_2H_3O_2$	69·0	19·8
$BaCl_2$..	48·6	$2KCl$	67·2	18·6
BaI_2	51·0	$2KI$	70·4	19·4
$MgSO_4$	19·2	$2K_2SO_4$	39·0	19·8
$MgCrO_4$	19·5	K_2CrO_4	38·9	19·4
$MgC_4H_4O_4$ ..	23·9	$K_2C_4H_4O_4$	45·1	21·2
$BaC_4H_4O_5$.. ..	20·1	$K_2C_4H_4O_5$	41·9	21·8
		Mean difference ..		20·7

		Difference.			
$\frac{1}{2}K_2SO_4$	19·0	KCl	33·6	14·6
$\frac{1}{2}MgSO_4$	9·6	$\frac{1}{2}MgCl_2$	24·4	14·8
$\frac{1}{2}K_2CrO_4$	19·4	KCl	33·6	14·2
$\frac{1}{2}MgCrO_4$	9·7	$\frac{1}{2}MgCl_2$	24·4	14·7
$\frac{1}{2}K_2SO_4$	19·0	KNO_3*	30·8	11·8
$\frac{1}{6}Al_2{}_3SO_4$	7·4	$\frac{1}{6}Al_2{}_3SO_4$	21·5	14·1
$\frac{1}{6}Al_2{}_3SO_4$	7·4	$\frac{1}{6}Al_2{}_6NO_3$	21·6	14·2
		Mean difference ..		14·0

i.e., Between the lowering produced in 100 grms. water by equal quantities of salts of the alkalies and alkaline earths there is a difference constant and equal to 10·5.

Also between the lowering produced by a monobasic acid and the corresponding salt of a dibasic acid there is a constant difference = 14.

1. From various reasons Raoult thinks that in a compound each atom exercises its own influence.

2. From consideration of the Tables above, he concludes that there is a constant proportion between the "partial depression" due to the electro-positive and electro-negative radicles of the same atomicity. For instance—

$$\frac{\text{Depression due to K}}{\text{,, ,, Cl}} = \frac{\text{Depression due to Mg}}{\text{,, ,, } SO_4}.$$

If we accept this hypothesis, we may re-write the equation thus—

$$\frac{\text{D. due to Mg}}{\text{,, } SO_4} = \frac{\text{D. due to K} - \text{D. due to } \frac{Mg}{2}}{\text{,, ,, Cl} - \text{,, ,, } \frac{SO_4}{2}}$$

$$\text{and this} = \frac{10·5}{14};$$

Also—

D. due to $MgSO_4$ = D. due to Mg + D. due to SO_4 = 19.

From these two equations we find—

Depression due to Mg = 8·1
,, ,, SO_4 = 10·9

Similarly—

,, ,, Na = 15·0
,, ,, Cl = 20·0

By similar calculations Raoult finds the partial depression due to each atom, and sees that they group nnder four heads.

Group.			
1	contains electro −ve radicles,	monatomic	At. Dp. = 20
2	,, ,, ,,	, diatomic	,, = 11
3	,, electro +ve radicles,	monatomic	,, = 15
4	,, ,, ,,	, diatomic	,, = 8

Having obtained these theoretical numbers it remains to see if they agree with the actual lowering produced. Raoult gives the following instances :—

	Calculated.	Observed.
KHO	35	35·3
Ba_2HO	48	49·7
HCl	35	36·7
$NaCl$	35	35·1
$BaCl_2$	48	48·6
$SnCl_4$	88	96·3
Al_2Cl_6	128	129·0
HNO_3	35	35·8
$NaNO_3$	35	34·0
Ba_2NO_3	48	40·5
$Al_2{}_6NO_3$	128	129·0
H_2SO_4	41	38·2
K_2SO_4	41	39·0
$MgSO_4$	19	19·0
$Al_2{}_3SO_4$	41	45·0

In a still later paper (*Annales de Chimie et de Physique*, July, 1886), M. Raoult has drawn the curves for the lowering of various salt solutions. In all cases he finds this rule to hold good :—

Trace the coefficient of lowering of the anhydrous substance to C = −1° to C = −4°, produce the part which is a straight line till it cuts the ordinate ; this value multiplied by the molecular weight gives the molecular lowering.

Thus, if C′ and C″ be the abscissæ, $\frac{C'}{P'}$ $\frac{C''}{P''}$ be the ordinates of any two points on the line, the length of ordinate cut off by the line will be—

$$\frac{\frac{C''}{P'}\,\frac{C'}{P''} = \frac{C'}{P''}\,\frac{C''}{P''}}{C'' - C'}$$

= 19 for organic salts
= 34·6 for salts containing monatomic bases + monatomic acids.
= 39·8 for salts containing monatomic bases + monad acids.
= 45·2 for salts containing diad bases + monad acids.
= 17 ,, ,, ,, + diad ,,
= 130 for chlorides of hexatomic radicles.

If, however, we work with dilute solutions, so that the freezing-point does not go much below −1°, a single determination suffices, and for practical purposes we have—

$$\text{Molec. lowering} = \frac{C}{P} \times M.$$

The employment of dilute solutions has other advantages :—1. Avoidance of arbitrary conclusions as to state (anhydrous or variously hydrated) of the body in solution. 2. Production of an appreciable quantity of ice without sensibly modifying concentration of solution. 3. The thermometer remains stationary a longer time.

It will be thus seen that Raoult's method affords a valuable means of determining :—

1. The molecular weight of a substance in the dissolved state.
2. The basicity of an acid.
3. The atomicity of a metal.

Among recent applications we may notice :—

1. Messrs. Brown and Morris on the carbo-hydrates (*Journal of the Chemical Society*, June, 1888). They show that the formula for cane-sugar, maltose, and milk-sugar is $C_{12}H_{22}O_{11}$ = 342 ; for dextrose, invert-sugar, arabinose, and mannitol $C_6H_{12}O_6$ = 180, and not multiples of these numbers.

2. Professor Ramsay on nitric peroxide (*ibid*). The supposed formula is N_2O_4 = 92. The number found for solution in acetic acid = 93·8

3. Dr. Morris Loeb, on iodine in differently coloured solutions (*ibid*, Oct., 1888). Dr. Loeb worked by the vapour-tension method. The same influence which lowers the freezing-point also raises the boiling-point. His conclu-

* In experiments with this salt I obtained for molecular lowering 34, making difference = 15, a number which accords fairly well with other differences.

sion is that molec. of iodine in reddish brown ethereal solution $=I_4$, in violet solution a less complex molecule.

Turning, now, to the more *physical* side of the question :—

If we have a tube, closed at the bottom by a membrane, pervious to water, but not to sugar, and this tube be partially filled with a solution of sugar, and then placed in an outer vessel of water. The solution will draw the water through the membrane ; the level of the liquid inside the tube will be considerably higher than that *outside* the tube. This will not continue indefinitely, but the quantity of water drawn in will vary with the concentration of the solution ; or,

Suppose an ordinary unglazed porcelain cell half filled with a solution of known percentage composition, and provided with a piston, and this be immersed in a vessel of water. Ordinarily speaking, the water would press into the inner vessel, but by applying external force to the piston, not only may water be prevented entering, but even some of that already in may be driven out. The force thus applied can be measured.

If just sufficient force be applied to prevent water either entering or leaving the inner tube, then this force must exactly balance the *osmotic pressure* due to the substance dissolved.

Pfeffer describes such experiments and finds that—

1. At constant temperature, pressure is proportional to concentration.

2. If quantity of sugar be constant, pressure × vol. of water = constant.

3. If pressure be constant, vol. × abs. temperature = constant.

I.e., For changes in temperature and density *osmotic* pressure varies in the same way as pressure in a gas, or that Boyle's and Charles's laws can be applied to solutions as well as to gases.

Similarly with Avagadro's law—so far as can be shown by direct experiments with semi-pervious membranes—unit volumes of solutions of equal molecular content have the same osmotic pressure, which is equal to the pressure of unit volume of a gas of the same molecular contents.

(This applies to weak solutions only, just as gaseous laws apply to perfect gases only, in which the molecules are so far apart that action between them may be neglected).

From these and other considerations — diminution of vapour-tension, &c., — Van't Hoff has concluded that *the condition of molecules in solution is strictly analogous to that of molecules in space* (*Zeitschrift für Physikalische Chemie*, vol. i., Nos. 9 and 11).

Mason Science College,
October, 1889.

ATOMIC CONSIDERATIONS.

By Dr. T. L. PHIPSON, F.C.S., &c

The little monograph intitled "Outlines of a New Atomic Theory," of which I issued a fourth edition in 1886, has been distributed to many eminent chemists in Europe and America, and to some of the public libraries. Nevertheless, I desire to refer once more to the subject, as numerous letters that reach me still express objections, from which it appears that the writers have, to a certain extent, misunderstood my meaning.

I have endeavoured to show that *t is not the atom* which differs from one substance to another—it is not a different nature of atom which causes the difference between two bodies, but the *difference of space between the atoms*. An element is a system of atoms. Atoms are all alike in size, weight, and form. The space between the atoms, which I term *phlogiston*, implies movement, heat, and electricity. The element which has the most phlogiston is the most energetic. The elements which make up organic nature are the most energetic of atomic systems.

Surely this is simple enough : the theory in question proclaims the *unity of matter* by showing that the atoms of iron, sulphur, hydrogen, iodine, &c., are all of equal size and weight — in fact, identical—and that elements are systems of atoms, all identical.

I cannot here follow up this theory into its various ramifications and consequences, nor have I done so very elaborately in the original monograph ; but if we admit the existence of atoms, as the most eminent chemical philosophers since the days of Dalton and Lavoisier have done, it appears to me that the above is the only rational conception of them. I must refer to my former paper for further considerations on this subject, and I trust that these few remarks will place my views in a clearer light to many correspondents who have endeavoured to raise objections to the theory.

London, December 2, 1889.

THE INFLUENCE OF SILICON ON THE PROPERTIES OF STEEL.*

(Concluded from p. 291).

The results of Mr. Bottomley's experiments were unfavourable. He found that the material had less susceptibility and more retentiveness than good soft iron, and that it had enormously less retentiveness than hard steel suitable for magnet-making.

Considerable attention having been given to the curious non-magnetic properties of manganese steel, the writer was led to make the approximate tests detailed in Table IV., to see if iron alloyed with other elements than manganese would also lose its magnetic susceptibility. From the list given it will be seen that practically manganese is the only exception ; for, as regards ferro-chrome, it is only when very high percentages of chromium are reached that the material is not susceptible.

Malleable Ferro-alloys.—Malleable compounds of iron with other elements so far experimented upon (including carbon, silicon, sulphur, phosphorus, chromium, tungsten, aluminium, and nickel) are strongly susceptible to magnetisation.

Alloys of manganese and iron, however, form an exception to this. As is now well known in manganese steel, as soon as the manganese exceeds 8 or 9 per cent the material is only attracted when in a finely divided state, such as drillings or powder, and with further increase of manganese even this slight susceptibility disappears. The same fact is noticed as regards the non-malleable compounds of iron and manganese. Alloys of iron, nickel, and manganese are also not susceptible.

2. *Cast State.*—As might be expected, the whole of the samples are very free from honeycombs ; but this soundness in the cast state is only acquired at the expense of toughness or ductility. As regards this freedom from honeycombs, it may be of interest to state here that although silicon does produce soundness in steel yet Mr. Holgate noticed that in making ferro-silicon of thirteen to fifteen per cent there is in casting an unusually large outburst of gas, and the pigs are exceedingly full of honeycombs. A sample is exhibited among the specimens accompanying this paper. In watching a cast of material of this percentage from the blast-furnace he noticed that when the exterior of the pigs became almost solid, and whilst the interior was still liquid, the metal began to boil up, and frequently for fifteen or twenty minutes some

* Third Report of the Committee, consisting of Professors Tilden and W. Chandler Roberts-Austen and Mr. T. Turner (Secretary), appointed for the purpose of investigating the Influence of Silicon on the Properties of Steel. Read before the British Association, Section B Newcastle Meeting.

TABLE IV.—*Table of Ferro-alloys, Showing their Magnetic Susceptibility.*

Name of alloy.	Special constituent.	Composition per cent (in some cases approximate). C p.c.	Si p.c.	S p.c.	P p.c.	Mn p.c.	Cr p.c.	W p.c.	Al p.c.	Fe p.c.	Magnetic susceptibility. In bulk.	In drillings or powdered slate.
Spiegeleisen ..	Manganese.	4¾	—	—	—	14	—	—	—	81¼	Attracted.	—
,, ..	,,	5½	—	—	—	36	—	—	—	58½	Not attracted.	Very slightly influenced.
Ferro-manganese	,,	7	—	—	—	82	—	—	—	11	,,	Very slightly influenced.
Ferro-silicon ..	Silicon.	1	16	—	—	1	—	—	—	82	Strongly attracted.	—
,, ..	,,	¾	20	—	—	2	—	—	—	77¼	,,	—
Silicon-spiegel ..	Manganese and silicon.	2	8	—	—	20	—	—	—	70	Easily attracted.	—
,, ..	Manganese and silicon.	1½	16	—	—	20	—	—	—	62½	Strongly attracted.	—
Ferro-chrome ..	Chromium.	4	1	—	—	1	8	—	—	86	,,	—
,, ..	,,	5	2	—	—	1	28	—	—	64	,,	—
,, ..	,,	5	1	—	—	1	63	—	—	30	Not attracted in the slightest.	Very slightly influenced.
,, ..	,,	5	2	—	—	1	79	—	—	13	Not attracted.	—
Ferro-aluminium	Aluminium.	1	1½	—	—	—	—	—	10	87½	Strongly attracted.	—
,,	,,	3	1½	—	—	—	—	—	12	83½	Very strongly attracted.	—
,,	,,	3	1½	—	—	—	—	—	18	77½	,,	—
,,	,,	1	1½	—	—	—	—	—	20	77½	Slightly attracted.	Strongly attracted.
Ferro-tungsten..	Tungsten.	4	1	—	—	1	—	40	—	54	Very strongly attracted.	—
Ferro-phosphorus	Phosphorus.	1	½	—	10	4	—	—	—	84½	Strongly attracted.	—
Ferro-sulphur ..	Sulphur.	½	¾	5	—	—	—	—	—	93¾	,,	Strongly attracted.

TABLE V.—*Table of Corrosion Experiments.*

		Percentage of silicon.	Strength of acid.	Length of immersion.	Loss p. c.	Colour after treatment.	Remarks.
Silicon steel (C).. ..	Bar	1·60	50 per cent.	21 days.	6·32	Very bright.	After being taken out of the acid and dried, the silicon steel and wrought iron appeared as if burnished, and retained their brilliancy for some time.
,, (E).. ..	,,	2·67	,,	,,	3·32	,,	
,, (G).. ..	,,	4·49	,,	,,	4·20	Very bright; soon dulled over, although carefully covered up.	
Ordinary mild steel ..	,,	—	,,	,,	7·48	Dull bright.	
Wrought iron	,,	—	,,	,,	4·47	Most brilliant.	
Silicon steel (E).. ..	Wire 20 B.W.G.	2·67	,,	,,	31·80	Very bright.	
Ordinary mild steel ..	,,	—	,,	,,	17·29	Dull.	
Ordinary wrought iron	,,	—	,,	,,	17·09	Very bright, like wrought bar.	
Manganese steel . ..	,,	Mn 12%	,,	,,	51·18	—	

Moisture Test.

		Percentage of silicon.	Weight before placing in moist atmosphere.	Weight after keeping 21 days in moist atmosphere.	Increased n weight.
Silicon steel (C)	Bar	1·60	20·634 grms.	20·644 grms.	0·01 grm.

The following table gives the specific gravities of the silicon steel, also ferro-silicon :—

TABLE VI.—*Specific Gravities.*

		Percentage of silicon.	Specific gravity.	Remarks.
Silicon steel (E)	Ingot.	2·67	7·38	—
,, ,, ...	Wire 20 B.W.G.	2·67	7 88	—
,, ,, (G)	Ingot.	4·49	7·54	—
Ferro-silicon	—	5·00	7·00	—
,, ,, ...	—	8·00	6·943	—
,, ,, ...	—	16·00	5·303	Doubtful.
Ordinary grey cast-iron . ..	—	—	7·10	—

cwts. of metal in each bed boiled over, this going on until the pigs were quite set and solid.

It would be interesting to know what is the cause of this outburst, and the composition of the escaping gases. It has been stated in metallurgical literature that in some hot overblown Bessemer charges silicon may be present in considerable percentages and yet the steel rise or boil over when poured into ingot-moulds.

Silicon steel pipes or settles to a much greater extent than ordinary steel, and this in itself is a considerable

disadvantage. Its fluidity when being poured is less than that of ordinary steel. The crystallisation or form of fracture of the lower percentages is somewhat like ordinary mild cast steel, but on exceeding about 2½ per cent Si a striking change occurs: the crystals become very large, glazed in appearance, and cleave somewhat after the nature of a spiegeleisen. As this large and marked crystallisation increases the material becomes exceedingly brittle, and if still further additions are made the appearance of the material approaches silicon pig-iron, and is non-malleable.

High percentages of silicon in the cast or unforged material cause a considerable increase in shrinkage or contraction. This point is already a difficult one with the steel-founder, who for many years has been on the horns of the dilemma that whilst silicon increases soundness it increases the tendency of castings to draw. In cast-iron this fact of silicon also increasing contraction has been noticed by Mr. Keep.

Also, as in the forged, so in the cast material, when the Si exceeds about two per cent and the peculiar crystallisation noticed in the samples exhibited commences, neither annealing nor water-quenching seems to have any effect in changing the structure.

It is well known that considerable difficulty is experienced in dissolving drillings of ferro-silicon; so tedious is the process that recourse is usually made to the sodium carbonate process. This is not requisite with silicon steel, which requires only the ordinary hydrochloric acid method. The silica residue is very clean and free from iron.

A considerable number of estimations have proved that the silicon is very uniform and homogeneous in this steel. Analyses taken from different parts of the same ingot and bar give results very similar to each other. No traces of graphite are noticed, the carbon always being present in the combined form. If the material analysed is in the form of drillings they keep their shape, the iron being dissolved out.

Experiments have been made with this steel in comparison with other material as regards its corrosion. The following table gives the time of immersion in the sulphuric acid, and the loss:—

Table VII.—*List of Samples Exhibited to Illustrate this Paper.*

Section I.—Samples of silicon steel in the cast state containing from 0·24 to 8·83 per cent of silicon.
Section II.—Samples of silicon steel in the forged state containing from 0·24 to 5·53 per cent of silicon.
Section III.—Test bars as mentioned in Table II.
Section IV.—Bending pieces given in Table II.
Section V.—Compression pieces given in Table III.
Section VI.—Samples of ferro-alloys to illustrate magnetic properties.
Section VII.—Silicon steel wire 2·67 per cent, 20 B.W.G.
Sample of ferro-silicon containing 16 per cent silicon, yet honeycombed.
Silica from silicon steel.
Also other samples.

PROCEEDINGS OF SOCIETIES.

CHEMICAL SOCIETY.

Ordinary Meeting, December 5th, 1889.

Dr. W. J. Russell, F.R.S., President, in the Chair.

Certificates were read for the first time in favour of Messrs. Frederick Graham Ansell, Wickwar, Gloucester; Sydney Hoare Collins, 19, Riverdale Road, Stoke Newington, N.; John B. Coppock, 126, Walton Street, Brompton, S.W.; Thomas Southall Dymond, 37, Hart Street, Bloomsbury; Cuthbert Chapman Gibbs, 3, Wyburn Villas, Surbiton; James Grant, Belmont Place, Chadderton, Oldham; Joseph H. Heywood, 23, Holland Street, Rochdale; James Guthrie, Mactaggart, Eskbank, Eltham, S.E.; James Sibun, 2, Lax Terrace, Norton, Stockton-on-Tees; Henry Wood Smith, B.Sc., Belmont, Higher Broughton, Manchester; John Stokes, Sarum House, Park Gate, Rotherham, Yorks; James Walker, 8, Windsor Terrace, Dundee; Sydney Russell Wells, 14, Girdlers Road, West Kensington.

The following were duly elected Fellows of the Society:—Messrs. Frank Thornton Addyman, Charles Frederic Baker, B.Sc., John Burgess, William Frederic Butcher, Frank Hill Perry Coste, David Brown Dott, Thomas William Dukes, Robert Stephen Edwards, B.A., James Kerr Erskine, John Simpson Ford, John Foggie, Harold Gripper, H. B. Helbing, Robert Edward Hughes, Eric Henry Jackson, James Robert Kaye, Henry Richard Kenwood, Frederick Thomas Knott, L. Napier Ledingham, G. B. Mason, James Braik Mason, Thomas Mercer, Joseph Alfred Nettleton, Wallace Christopher Nickels, J. T. Norman, James Gordon Parker, Alfred Edridge Pike, William Ping, Frederick Quincke, Ph.D., Sydney Steel, Sidney Augustus Sworn, John Bishop Tingle, Willis G. Tucker, M.D., Daniel Walker, B.Sc., William Whitehouse, Matthew Wittam, Basil P. Wigan, John Wiltshire, John Wilkie.

The following papers were read:—

102. "*Compounds of Phenanthraquinone with Metallic Salts.*" By Francis R. Japp, F.R.S., and Alfred E. Turner.

The authors have obtained several double compounds of phenanthraquinone with metallic salts, viz.,—

$$C_{14}H_8O_2 \cdot ZnCl_2,$$

which forms dark reddish brown needles, not melting even above 300°; $(C_{14}H_8O_2)_2HgCl_2$, crystallising in red, obliquely truncated prisms, melting at 222—223°; and $(C_{14}H_8O_2)_2HgCy_2$, which also forms red crystals, melting like the foregoing, at 222—223°. Oxysalts do not unite with phenanthraquinone.

They have prepared a similar compound (not analysed) from mercuric chloride and β-naphthaquinone; but could not obtain double compounds from benzoquinone, α-naphthaquinone, anthraquinone, diacetyl, and benzil. It would therefore appear that compounds of this class are derivable only from orthoquinones, and not from paraquinones, or open-chain α-diketones.

The intense colour of the double compounds in question indicates that in them the quinone preserves its distinctive character. In this respect they differ from the colourless compounds of the ortho-quinones with hydrogen sodium sulphite, the formation of which involves a reduction, and which are to be regarded as quinol-derivatives.

Discussion.

Dr. Armstrong remarked that the preparation and study of compounds such as the authors described were of importance in elucidating the nature of molecular compounds, and as affording valuable material for the discussion of the problem of valency. It was highly remarkable that the compounds were so much more intensely coloured than phenanthraquinone. Were their solutions equally coloured, and did the colour vary much with the concentration; would it not be possible by observation of the colour of solutions of varying strength to determine to what extent the compounds existed in solution, and at the same time to apply to them the Raoult freezing-point method?

Dr. Japp, in reply, said that the intense colour of the compound was at once apparent on mixing hot solutions of zinc chloride and of phenanthraquinone in glacial acetic acid, but the compound immediately begins to separate out; it was so sparingly soluble that it would not be possible to determine the molecular weight by

Raoult's method. In preparing the mercury compounds acetone was used as solvent; like the zinc compounds they were decomposed by water and also by acetic acid.

Mr. Chapman said that on mixing solutions of dextrose and of nickel oxide in ammonia, a dark green liquid was obtained of the colour of the compound, which subsequently crystallised out.

103. "*Action of Aldehyds and Ammonia on α-Diketones.*" By G. H. Wadsworth, Associate of Normal School of Science.

The author has studied the action of various aldehyds and ammonia on diacetyl, and has obtained the following glyoxalines:—

With benzaldehyd: *phenyldimethylglyoxaline*,—

$$C_{11}H_{12}N_2;$$

slender needles, melting at 230—234°.

With salicylaldehyd: *ρ-hydroxyphenyldimethylglyoxaline*, $C_{11}H_{12}N_2O$; satiny needles, melting at 218°.

With cinnamic aldehyd: *cinnamenyldimethylglyoxaline*, $C_{13}H_{14}N_2$; warty crystals, melting at 201—202°.

In addition, *cinnamenyldiphenyleneoxazole*, $C_{23}H_{15}NO$, has been prepared by the action of cinnamic aldehyd and ammonia on phenanthraquinone; slender yellow needles, melting at 171—172°.

104. "*Phenylhexamethylene Derivatives.*" By F. Stanley Kipping, Ph.D., D.Sc., and W. H. Perkin, jun., Ph.D.

The authors find that on boiling phenyldehydrohexonecarboxylic acid,—

$$C_6H_5\cdot C{=\!=}C\cdot COOH$$
$$O< \qquad >CH_2,$$
$$CH_2\cdot CH_2$$

with water it yields benzolybutyl alcohol,—

$$C_6H_5\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$$

and carbon dioxide. This alcohol crystallises from water in large flat plates, which melt at 40—41°: although stable under ordinary conditions, when placed over sulphuric acid, the crystals rapidly disappear and are converted into oily drops of phenyldehydrohexone.

The *hydroxime*,—

$$C_6H_5\cdot C(N\cdot OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$$

is readily obtained by the interaction of benzoylbutyl alcohol, hydroxylamine hydrochloride, and excess of potash in alcoholic solution. It crystallises from benzene in colourless microscopic plates which melt at 56—57°.

Phenylpentylene glycol,—

$$C_6H_5\cdot CH(OH)\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot OH,$$

prepared by the action of an excess of sodium amalgam on a dilute alcoholic solution of benzoylbutyl alcohol, crystallises from benzene in colourless concentrically-grouped needles, which melt at 54°; it is readily soluble in ether, alcohol, benzene, and hot water, but only sparingly in light petroleum.

Phenylpentylene dibromide,—

$$C_6H_5\cdot CHBr\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2Br,$$

is best prepared by dissolving the glycol in chloroform and gradually adding a slight excess of phosphorus pentabromide; it is a slightly brownish-coloured disagreeably-smelling oil, which is insoluble in water. It is readily acted upon by ethylic sodiomalonate, forming ethylic phenylhexamethylenedicarboxylate,—

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot C_6H_5 \\ |\qquad\quad | \\ CH_2\cdot CH_2\cdot C(CO_2Et)_2 \end{array}.$$

By heating the oily acid obtained from this ethereal salt at 180—200°, *phenylhexamethylene monocarboxylic acid*,—

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot C_6H_5 \\ |\qquad\quad | \\ CH_2\cdot CH_2\cdot CH\cdot COOH \end{array}$$

is produced. This acid is best purified by conversion, first into the barium salt and then into the crystalline ammonium salt. It crystallises from light petroleum in short thick prisms which melt at 104—105°; it is readily soluble in ether, alcohol, chloroform, and acetone, only moderately easily in cold light petroleum, difficultly soluble in water.

On boiling an alcoholic solution of phenylpentylene dibromide and ethylic sodacetoacetate the two substances readily interact, yielding ethylic acetylphenylhexamethylenecarboxylate,—

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot C_6H_5 \\ |\qquad\quad | \\ CH_2\cdot CH_2\cdot C(CO\cdot CH_3)\ COOC_2H_5 \end{array}.$$

On hydrolysis this ethereal salt yields phenylhexamethylenecarboxylic acid (m. p. 104—105°), identical with the acid described above, and *phenylhexamethylenemethylketone*,

$$\begin{array}{l} CH_2\cdot CH_2\cdot CH\cdot C_6H_5 \\ |\qquad\quad | \\ CH_2\cdot CH_2\cdot CH\cdot CO\cdot CH_3 \end{array}.$$

This substance crystallises in colourless needles, melting at 78—79°, and distils at about 187—190° under 40 m.m. pressure without decomposition; the hydroxime produced by treating it with hydroxylamine and excess of potash in alcoholic solution is a thick colourless oil, which could not be obtained in a crystalline condition.

105. "*Diphenylfurfuran.*" By W. H. Perkin, Jun., Ph.D., and Aug. Schloesser, Ph.D., M.Sc.

Ethylic dibenzoylsuccinate,—

$$\begin{array}{l} C_6H_5\cdot CO\cdot CH\cdot CO_2Et \\ | \\ C_6H_5\cdot CO\cdot CH\cdot CO_2Et \end{array},$$

is best prepared by treating an ethereal solution of ethylic benzoylacetate with the calculated quantity of sodium (1 atomic proportion) in the form of fine wire, and then adding a slight excess of iodine. It is converted by concentrated sulphuric acid into ethylic diphenylfurfurandicarboxylate,—

$$\begin{array}{l} C_6H_5\cdot C{=}C\cdot CO_2Et \\ O< \quad | \\ C_6H_5\cdot C{=}C\cdot CO_2Et \end{array};$$

on hydrolysis it yields the dicarboxylic acid.

Diphenylfurfuranmonocarboxylic acid,—

$$\begin{array}{l} C_6H_5\cdot C{=}CH \\ O< \quad | \\ C_6H_5\cdot C{=}C\cdot COOH \end{array},$$

is obtained, together with diphenylfurfuran, on heating the dicarboxylic acid to about 250°. It crystallises from benzene in short colourless needles which melt at about 214°. It does not yield a hydroxime when treated with hydroxylamine, neither is it affected by boiling with acetic anhydride.

Diphenylfurfuranmonocarboxylic acid tetrabromide, $C_{17}H_{12}Br_4O_3$, is produced when the finely-divided acid is exposed to the vapour of bromine as a hard crystalline mass, almost insoluble in solvents.

Diphenylfurfuran—

$$\begin{array}{l} C_6H_5\cdot C{=}CH \\ O< \quad | \\ C_6H_5\cdot C{=}CH \end{array},$$

crystallises from light petroleum in pearly plates which melt at 81° and distil at a high temperature almost without decomposition. It is very readily soluble in benzene and alcohol, but sparingly soluble in cold light petroleum.

Diphenylfurfuran tetrabromide, $C_{16}H_{12}Br_4O$. This compound is readily produced when diphenylfurfuran is exposed for some hours to the action of bromine-vapour. The resulting dark-coloured mass becomes almost colourless when placed over caustic potash; when purified by re-crystallisation from benzene, it forms beautiful satiny plates melting at 190°.

Oktohydrodiphenylfurfuran, $C_{16}H_{20}O$, is produced when a boiling alcoholic solution of diphenylfurfuran is treated with an excess of sodium. It is a slightly yellowish-coloured oil which boils at 150—155° under 110 m.m. pressure.

PHYSICAL SOCIETY.

December 6, 1889.

Prof. Reinold, F.R.S., President, in the chair.

Mr. J. W. Swan was elected a member of the Society.

The following communications were read:—

"*On the Electrification of a Steam-Jet.*" By Shelford Bidwell, F.R.S.

The author showed that the opacity of steam issuing from a nozzle is greatly increased by bringing electrified points near it, and that its colour is changed to orange brown. Electrified balls and discs, when placed in the steam, produce similar effects, and when these are connected with an influence machine at work the decolouration of the jet rapidly responds to each spark. On examining the absorption-spectrum of the unelectrified jet, little or no selective absorption was detected, but, on electrification, the violet disappeared, the blue and green were diminished, and the orange and red remained unchanged. From these results the author concludes that electrification causes an increase in the size of the water particles in the steam, from something small compared with the wave-length of light, to about 1-50,000th of an inch in diameter. Allied phenomena with water-jets have been observed by Lord Rayleigh, who found that a straggling water-jet is rendered much more coherent by bringing a rubbed stick of sealing-wax near it.

These observations are of considerable meteorological interest, for the steam-jet phenomena go far towards explaining the cause of the intense darkness of thunder-clouds, and of the lurid yellow light with which that darkness is frequently tempered.

After making his experiments the author learnt that similar observations had recently been made by the late Robert Helmholtz, who viewed the steam-jets by reflected light against a dark background. On electrification the jets became much better defined, and presented diffraction colours. Luminous flames also produced similar effects, and Mr. Bidwell has found that glowing touch-paper is equally efficient. Helmholtz conjectures that the sudden condensation may be due to moleculur tremors or shock imparted by the electrification, upsetting the unstable equilibrium of the supersaturated vapour, just as a supersaturated saline solution is suddenly crystallised when disturbed. Another hypothesis suggests that condensation is caused by the introduction of solid matter into the jet by the exciting cause, thus providing nuclei upon which the vapour may condense.

On reading Helmholtz's paper the author tried the effect of gas-flames on water-jets, and found that, when luminous, they influenced the jet considerably, whereas non-luminous flames had no appreciable effect. He also found that luminous flames are positively electrified, and demonstrated this before the meeting.

Prof. Rücker thought the surface-tension of the films surrounding the water-jets might be lowered by the presence of a burning substance, and that the smoke from the touch-paper used in some of the experiments on steam-jets would introduce solid particles and facilitate condensation.

Mr. Richardson enquired whether a red-hot iron had any effect.

Dr. Fison said he had made experiments on the electrification of flame, and found that potentials varying from +2 volts to $-1\frac{1}{2}$ volts could be obtained in the region within and surrounding a Bunsen flame.

Prof. S. P. Thompson commented on the contrast between Mr. Bidwell's experiments and those of Dr. Lodge on the dissipation of fogs by electricity, and also asked whether the colour of the jet depended on the length of spark produced by the machine.

Prof. Forbes thought a crucial test between the two hypotheses of Helmholtz could be obtained by trying the experiment in a germless globe.

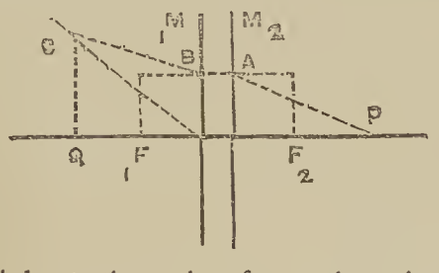
The President said he had recently noticed that gas-flames were electrified.

Mr. Bidwell, in reply, said he ought to have mentioned that the effect of flames on jets may be due to dirt, for if soap or milk be added to the water in the steam-generator, no effect is produced by electrification or flame. As to change of colour with spark-length, little (if any) variation is caused thereby. He had not tried whether a red-hot iron produced any effect on a steam-jet.

"*Notes on Geometrical Optics: Part* II." By Prof. S. P. Thompson, D.Sc.

Three notes were presented, the first of which dealt with the geometrical use of "focal circles" in problems relating to lenses and mirrors, and to single refracting surfaces. By "focal circles" the author means the circles having the principal foci as centres, and whose radii are equal to the focal lengths. By their use the point conjugate to any point on the principal axis is readily determined. One construction for a mirror is to draw a tangent to the focal circle to a point, P, on the axis; the foot of the perpendicular to the axis, drawn through the point of contact, gives the point conjugate to P. When applied to a thin lens, a tangent is drawn, as above, to one focal circle, and the line joining the point of contact with the centre of the lens is produced to meet the other focal circle; a perpendicular to the axis from the remote point of intersection gives the conjugate point. Modifications applicable to thick lenses and single refracting surfaces were also given.

In his second note the author treated similar problems by the aid of squares drawn on the principal focal distances, the constructions being remarkably simple, as will be seen by the figure, in which M_1 M_2 represent the principal planes of a thick lens, F_1 F_2 its principal foci, and P and Q are conjugate points. The line B C is drawn parallel to P A.



In the third note the paths of rays through prisms are determined by the aid of imaginary planes representing the apparent position of the plane bisecting the dihedral angle of the prism when viewed through its two faces. Just as in problems on thick lenses in which the part between the principal planes may be supposed removed, so, when dealing with prisms, the part between the imaginary planes above referred to may be supposed non-existent. In another method of treatment the apparent positions of points outside the prism, when viewed from inside the prism, are made use of, and their application to illustrate dispersion was pointed out.

Mr. C. V. Boys asked whether the latter construction could be used to show why the slit of a spectroscope appears curved.

"*On the Behaviour of Steel under Mechanical Stress.*" By Mr. C. H. Carus-Wilson.

This was an enquiry into the properties of steel as illustrated by the *stress-strain* curves given in automatic diagrams from testing machines, and by magnetic changes which take place during testing.

After pointing out that the permanent elongation of a

bar under longitudinal stress consists of a sliding combined with an increase of volume, the author showed that the "yield" is caused by the limit of elastic resistance (ρ) parallel to one particular direction in the bar (generally at 45° to the axis), being less than along any other direction. When this lower limit is reached, sliding takes place in this direction until the hardening of the bar caused thereby raises the limit of elastic resistance in the direction referred to, to that of the rest of the bar, after which the stress must be increased to produce further permanent set.

From considerations based on the stress-strain curves of the same material when hardened to different degrees by heating and immersion, &c., it was concluded that the increase of (ρ) during "yield" is the same for all the specimens, and that the "yield" is a measure of the "hardness."

The question of discontinuity of the curves about the "yield point" was next discussed, and evidence to the contrary given by specimens which show conclusively that the yield does not take place simultaneously at all parts of the bar, but travels along the bar as a strain-wave. In these specimens the load had been removed before the wave had traversed the whole length, and the line between the strained and unstrained portions could be easily recognised. As additional evidence of continuity, the close analogy between the *stress-strain* curves of steel of various degrees of hardness, and the isothermals of condensible gases at different temperatures when near the point of liquefaction was pointed out; the apparent discontinuity in the latter probably being due to the change from gas to liquid taking place piecemeal throughout the substance (see Prof. J. Thomson, *Proc. Roy. Soc.*, lxxi., No. 130).

In seeking for an explanation of the hardening of steel by permanent strain, the author was led to believe this due to the displacement of the atoms within the molecules of the substance. To test this hypothesis, experiments on magnetisation by stretching a bar in a magnetic field were made; these show that the magnetisation increases with the stress up to the "yield point," and is wholly permanent when approaching that point. On comparing his results with Joule's experiments on the elongation of loaded wires produced by magnetisation, the author infers that there are two kinds of elongation; firstly, that produced by relative motion of the molecules; and secondly, an elongation resulting from a straining of the molecules themselves. To this latter straining the hardening by permanent strain is attributed, and this view seems compatible with the results of Osmond's researches on the hardening of steel.

Mr. F. C. Hawes's paper was postponed.

ROYAL INSTITUTION OF GREAT BRITAIN

General Monthly Meeting, Monday, December 2, 1889.

Sir James Crichton-Browne, M.D., LL.D., F.R.S., Treasurer and Vice-President, in the Chair.

The following were elected Members of the Royal Institution:—Messrs. Charles Vernon Boys, F.R.S., A.R.S.M.; Frederick Bayard Wiggins; and Alfred Fernandez Yarrow, M.Inst.C.E.

The Managers reported that they had re-appointed Professor James Dewar, M.A., F.R.S., as Fullerian Professor of Chemistry.

Electro-conductivity of the Eiffel Tower and its Earth Connections.—A. Terquem.—The totality of the lightning conductors of the Eiffel tower, fitted up according to the indications of MM. Becquerel, Berger, and Mascart, may be considered as very perfect and as likely to exert a protective influence over a considerable radius. —*Comptes Rendus*, Vol. cix., No. 23.

NOTICES OF BOOKS.

Ammonia and Ammonium Compounds: Comprising their Manufacture from Gas Liquor and from Spent Oxide (with the Recovery from the latter of the By-products, Sulphur, Sulphocyanides, Prussian Blue, &c.). Special Attention being given to the Analysis, Properties, and Treatment of the Raw Materials and Final Products. A Practical Manual for Manufacturers, Chemists, Gas-Engineers, and Drysalters. From Personal Experience, and Including the most Recent Discoveries and Improvements. By Dr. R. Arnold. Translated from the German by Harold G. Colman, Ph.D., M.Sc. London: Sampson Low, Marston, Searle, and Rivingtons.

This valuable work commences with the chemistry of ammonia. Here we find it declared, contrary to the recent results of M. Berthelot and other chemists, that plants have no power of absorbing atmospheric nitrogen. It is very desirable that this vexed question should come to a definite settlement. The author adds that probably "plants can only assimilate the nitrogen from nitric acid, and that the ammonia is first oxidised to that compound. This view is controverted by some recent researches of A. Muntz, which seem to show that ammonia can be utilised by plants as such.

In his account of the salts of ammonium, Dr. Arnold states that sal-ammoniac was originally known as *sal-armeniacum*, from having been brought into commerce by Armenian merchants. The name was subsequently changed to *sal-ammoniacum*, a name which had first been given to the sodium chloride found near the ruins of the Temple of Jupiter Ammon, in the Libyan Desert.

We find it said, on the authority of Woehler, that the deep black ink formed on mixing tincture of galls with ammonium meta-vanadate is not permanent.

For rapid estimations of ammonia the author recommends Knop's "azotometer," which is here described and figured.

In the second chapter, the author proceeds to the manufacture of ammoniacal salts. In speaking of the common method of determining the value of a gas liquor by the number of ozs. of pure sulphuric acid which it requires per gallon for saturation, Dr. Arnold reminds us that this test only indicates the amount of volatile ammonia. For determining the specific gravity he mentions, along with Twaddell's hydrometer, Fleischner's "densimeter." "In this instrument the specific gravity is obtained at once by putting the figure 1 and the decimal point before the number of degrees recorded." An instrument having this scale was in use in the Lancashire alkali district as far back as 1858. For a complete analysis of gas liquor the author gives the method of S. Dyson.

For the transport of sulphuric acid the author recommends iron tanks, in preference to the 17—20 gallon carboys employed in England. A 20 gallon carboy, especially in the case of so heavy a liquid as monohydrated sulphuric acid, is far too heavy to be manipulated with convenience and safety.

For obtaining ammonia from gas liquor, the continuous still of Feldmann is recommended.

After giving instructions for the analysis of ammonium sulphate, the author speaks of the competition between this salt and Chili saltpetre for manurial purposes. This circumstance has rendered the manufacture of ammonia much less profitable than it was until recently.

After describing the manufacture of the hydrochlorate, carbonate, and nitrate, Dr. Arnold passes to the sulphocyanide. The recovery of this salt from gas liquor has not been very widely practised, though R. Gasch thinks it ought to be more generally attempted, in preference to its manufacture from spent oxide.

The lime mud, and especially the waste liquor, from ammonia works are characterised as troublesome products

for which no satisfactory method of disposal has been elaborated.

The remainder of the work is devoted to the utilisation of spent oxide, and with appropriate tables. There is also a bibliography of the subject, and a list of patents, German and English, relating to the manufacture of ammonia and of its by-products.

The work must be pronounced thoroughly practical and calculated to be of great value to the interests concerned.

Facts and Observations concerning Railway Rates, and Practical Suggestions relating to the Classification of Merchandise Traffic by the Board of Trade. By J. W. Gray. London and Manchester: J. Heywood.

Mr. Gray argues that the railway companies, by training up in their goods offices thousands of young men in deceptive arts, are largely responsible for the corruption existing in the commercial world. He shows that, in spite of the recent Act of Parliament, the railways still carry alien manufactures and produce over their lines at lower rates than home traffic.

One of the remedies for such mischief the author does not mention: the enactment, as suggested by the late Peter Spence, of Manchester, that no railway company be permitted to own, lease, or work any canal or other channel of navigation.

Letts's Diaries for 1890. London, Paris, New York, and Melbourne: Cassell and Company (Limited), 1889.

These Diaries have been before the public for upwards of a century, and their convenience and variety have kept pace with the growing demands of the age.

The Rough Diaries, Nos. 31 and 48, interleaved with blotting-paper, the former giving three days to a page, and the latter half a page to a day, are perhaps the most useful kinds for the desk of the analytical chemist and man of science. The Blotting-pad Diary, foolscap size, is also very useful for the writing table. Among the smaller sizes may be mentioned the Office Diary, suitable for smaller memoranda and appointments, the Pocket Diaries, Nos. 26, 18, and 23 D, and the Medical Diary. The latter has proved to be so useful to medical men that we are tempted to ask whether it would not be worth the attention of the publishers to compile a similar pocket-book for chemists and physicists.

CORRESPONDENCE.

STANDARD SOLUTION OF FERRIC SALTS WITHOUT TITRATION.

To the Editor of the Chemical News.

Sir,—In the Chemical News (vol. lx., p. 293), H. N. D., Dublin, points out that "the use of ferrous ammonium sulphate for the preparation of standard iron solutions is not new." I beg to state that I did not claim it as such; I merely pointed out the use of H_2O_2 as the oxidising agent in preparing a pure ferric standard solution from the above salt, on account of the facility with which the excess of oxidising agent can be removed.

I should be extremely obliged if H. N. D. would point out the page and line in "Sutton," 1863, or any later edition, where the method is given.

I may state that I have not noticed this method given in any book, or should not have published it.—I am, &c.,

W. French.

Cambridge.

"NOTES ON QUALITATIVE ANALYSIS."

To the Editor of the Chemical News.

Sir,—Pardon my referring to your notice of my "Notes on Qualitative Analysis" (Chem. News, lx., 245).

I agree with you that "students who have not access to a well-stocked library" would certainly be unwise to attempt work with such a book; but with students such as we have here, and with the facilities for reference we possess, there is no possible doubt but that most excellent results are obtained by forcing a thorough examination of references, and then basing the daily interrogations upon those references. I go a step further in the attempt to make students think for themselves, by assigning them such cases from my private work as may come within the limits of their abilities. In such instances the student is brought into direct communication with the parties desiring the work done, and he writes and signs the final report. Such work being always done gratis, there is no difficulty in securing a sufficient supply.—I am, &c.,

William P. Mason.

Rensselaer Polytechnic Institute,
Department of Analytical Chemistry,
Troy, N.Y., December 4, 1889.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 23, December 2, 1889.

Formenic Fermentation of Farmyard Manure.—Th. Schlœsing.—During the formenic fermentation of farmyard manure at the temperature of 52°, no gaseous nitrogen is produced from a decomposition of nitrogenous compounds. There is no nitrogenous compound formed by the fixation of ammonia upon organic matter. On the contrary, nitrogen escapes from organic combinations and makes its appearance in the state of ammonia. The organic substance becomes impoverished in carbon more than in oxygen, whilst the proportion of hydrogen remains approximately the same. Water takes part in the decomposition of the organic substance, and supplies to the carbon at once oxygen and hydrogen. M. Berthelot made some remarks on the above paper from a thermochemical point of view, and called attention to the analogies between the formenic and the alcoholic fermentation.

Method of Measuring the Spherical and Chromatic Aberration of Object-Glasses for the Microscope.—C. J. A. Leroy.—In the present state of construction the problem of achromatism may be considered as solved, whilst this is far from being the case with aplanetism. The correction of spherical aberration requires, therefore, to be studied for the improvement of objectives.

New Researches on the Preparation and the Density of Fluorine.—Henri Moissan.—The apparatus now employed by the author is much longer than the one used at first. The U-tube of platinum in which the electrolysis is produced has a capacity of 160 c.c., and it can contain, during the preparation, about 100 c.c. of hydrofluoric acid. To prevent vapours of hydrofluoric acid from being carried over there is attached a small worm of platinum serving as a condenser, and kept in methyl chloride at about −50°. As hydrofluoric acid boils at 19·5°, almost all this compound is kept back in a liquid state at the bottom of the worm. After passing through the worm the gas traverses two platinum tubes filled with fragments of sodium fluoride. This compound energetically absorbs any hydrofluoric acid present. The

fluorine, thus purified, does not produce fumes in dry air, and it can be conveyed into the receivers by means of small flexible tubes of platinum. The specific gravity of pure fluorine has been determined as 1·26, which is very close upon the theoretical figure.

Certain Facts relative to the Analysis of Sugars.—E. Jungfleisch and L. Grimbert.—Weak acids do not modify the rotatory power of levulose, whilst the strong acids increase it to an important extent, though variable according to circumstances. This fact has a considerable influence upon the accuracy of the various methods used for the analysis of sugars. This is the case with the classical method of Clerget, in which the analysis of a mixture of saccharose and inverted sugar is effected with the polarimeter and by inversion. At the origin of this method Peligot and Dubrunfaut objected that it raised the weight of the saccharose. Experience has confirmed this opinion, and the authors detect a serious irregularity in the principle of the method.

Zeitschrift fur Analytische Chemie.
Vol. xxviii., Part 4.

The Determination of Extract in Wines by the Indirect Method.—E. Egger.—This memoir is not susceptible of reproduction.

Distinction of Fruit and Carrot "Kraut."—J. König and M. Wesener.—The substance known as "kraut" in Western Germany and "muss" in the East is a solution or extract of fruit, or of turnips, carrots, &c., evaporated down to a paste, and eaten upon bread. The article prepared from fruit, being much more valuable than that made from roots, is sometimes sophisticated with the latter. As "kraut" is not known in England, a reproduction of this memoir would have no interest for our readers.

Determination of Nitrogen by the Kjeldahl Method.—F. Martinotti.—The author's results seem to him to justify the following conclusions:—(1) For the determination of organic and ammoniacal nitrogen in manures in the absence of nitrates, the Kjeldahl method is preferable to that of Will-Varrentrapp, which has hitherto been in use. (2) For the determination of the total nitrogen in presence of nitrates, the Kjeldahl-Jodlbauer (see *Zeitschrift*, xxvi., 92) method is not suitable, as it does not give accurate results and requires too much time. It is better first to destroy the nitrates by heating with concentrated hydrochloric acid and ferrous chloride, and to determine them separately in another portion.

The Determination of Nitric Nitrogen by Kjeldahl's Method.—Dr. Otto Foerster.—This paper will be inserted in full as early as possible.

Purification of the Colouring-Matter of Litmus.—Dr. Otto Foerster.—Commercial litmus of the best quality is first extracted in the cold with common litmus, then digested with water, and the solution filtered and evaporated down. The residue is again dissolved in water, filtered, and the filtrate precipitated with absolute alcohol to which a little glacial acetic acid has been added. The precipitate is collected on a filter and washed with alcohol, when a violet fluorescent colouring-matter remains in solution. The residue is again dissolved in water, and the precipitation, filtration, and washing are repeated, when a red colouring-matter remains in solution, which, if dissolved in an alkali, appears violet. On a repetition of this process only a small quantity of colouring-matter remains in solution. The precipitate on the filter is dried and repeatedly moistened with alcohol to expel acetic acid. The precipitate is now again dissolved in water and the solution is filtered. The colouring-matter is finally precipitated with weak ammoniacal alcohol, collected on a filter, washed with pure alcohol, dried, and is ready for use.

A Contribution to the Determination of Ammonia by Distillation.—W. M. Stein and Paul W. Schwarz.

A New Apparatus for Titration.—Victor Hölbling.

Separation of Ethereal Solutions from Watery Liquids.—A. Gawalowski.—These three papers cannot be usefully reproduced without the accompanying cuts.

The Rise of the Zero-Point in Mercurial Thermometers made by Jena Normal Glass.—F. Allihn.—The glass in question contains:—

Zinc oxide	7
Calcium oxide..	7
Soda	14½
Alumina	2½
Boric acid..	2
Silica..	67
	100

Thermometers made of this glass showed an average depression of 0·05°; those of Thuringian glass, one of 0·4°; and those of English crystal glass (containing lead), 0·15°.

Gas-generating Apparatus with a Constant Efflux of Liquid.—Theodore Breyer.—This memoir requires the accompanying illustration.

On Horse-Fat.—Already inserted.

Quantitative Determination of Galactose.—E. Steiger.—This paper depends chiefly on the tables present.

Determination of Carbon in the Irons of Commerce.—L. Blum.—Already inserted.

Precipitation of Magnesia.—L. Blum.—Already inserted.

A Source of Error in the Separation of Small Quantities of Manganese from an Excess of Lime by Means of Ammonium Sulphide.—L. Blum.—Already inserted.

Wormwood Wine appears to be made by digesting wormwood in the local red wine.

Use of Kaolin Balls and of Salet's Pipette in Gas Analysis by Bunsen's Process.—N. Bunge (*Journal der Russisch Phys. Chem. Gesell*).—This paper requires the three accompanying figures.

A Collection of the Specific Gravities of Aqueous Solutions.—Dr. G. Th. Gerlach.—Nearly sixty pages of tables.

Revue Universelle des Mines et de la Metallurgie.
Series 3, Vol. vi., No. 3.

This issue contains no chemical matter.

Bulletin de la Société Chimique de Paris.
Series 3, Vol. ii., Nos. 7 and 8.

Combustion-Heats of Isodibutylene and Isotributylene.—M. Malbot.

The Analysis of Methylanilines.—F. Reverdin and Ch. de la Harpe.—A criticism of a recent paper on this subject published by H. Giraud.

Determination of the Carbonic Acid of the Carbonates in Arable Soils.—J. A. Muller.—A volumetric process, executed with a modification of Scheibler's apparatus.

MEETINGS FOR THE WEEK.

Monday, Dec. 23rd.—Medical, 8.30.
Friday, 27th.—Quekett Club, 8.
Saturday, 28th.—Royal Institution, 3. "Electricity," by Professor A. W. Rücker, M.A., F.R.S.

THE CHEMICAL NEWS.

Vol. LX. No. 1570.

RESEARCHES ON THE CHEMISTRY OF THE CAMPHORIC ACIDS.*

By J. E. MARSH, B.A.,
Demonstrator of Organic Chemistry at the University Laboratory, Oxford.

For some time past I have been engaged in the study of some derivatives of camphor, with the view of determining, if possible, with some degree of certainty the constitution of that body. I do not propose to enter now into any account of the present state of our knowledge as to the chemistry of camphor, but at once to bring forward something of my own experience on this subject.

Of part of the results which I have obtained I gave a brief account at the meeting of the British Association last year at Bath. This account had reference chiefly to some further evidence of the relationship of camphor to hexahydrometaxylene, and to the products of oxidation of camphoric acid by means of an alkaline solution of potassium permanganate. These researches were not published, and are not even yet completed.

On the other hand, I have made some additional experiments which I am anxious to bring forward now, as it may be some time before the whole series is finished.

The experiments to be described have reference to certain processes which resulted in the preparation of a new camphoric acid; and the remarkable properties of this acid, contrasted with those of the ordinary camphoric acid, throw considerable light on the nature of the isomerism subsisting between these bodies.

Camphoryl Chloride.

I have had occasion to prepare considerable quantities of camphoryl chloride, $C_{10}H_{14}O_2Cl_2$, by the action of pentachloride of phosphorus on ordinary camphoric acid. Camphoryl chloride was obtained originally by Moitessier (*Comp. Rend.*, lii., 871), but only as a crude product, which he found to decompose on distillation. The substance may, however, be readily purified by distillation *in vacuo*, when it distils about 140° C. under 15 m.m. pressure. There appears to be no difference in the product of the reaction however much pentachloride of phosphorus is used, provided the temperature be not raised above that of boiling water.

Chlorocamphoryl Chloride.

If, however, camphoric acid is heated with a large excess of pentachloride of phosphorus on a sand-bath in a flask provided with a reflux condenser, a new body of the formula $C_{10}H_{13}Cl_3O_2$, viz., chlorocamphoryl chloride, is obtained. A further account of this body and its transformations I will reserve for a future publication.

The camphoryl chloride was prepared in order to attempt to reduce it to the lactone similar to the lactones obtainable from phthalyl and succinyl chlorides. It was not found possible to obtain a lactone under the various conditions of experiment from time to time adopted.

Action of Water on Camphoryl Chloride.

Circumstances, however, led to the consideration of a more simple reaction, namely, the action of water on camphoryl chloride. Moitessier had stated that this reaction was such as to give back camphoric acid. He means, presumably, the original dextro-rotatory acid, as he does not mention more than one. This acid is, in fact, formed, as will be shown subsequently, but only in very small quantity, and can only be separated from and recognised among the other products of the reaction after special treatment.

If camphoryl chloride obtained from ordinary dextro-camphoric acid is added gradually to about ten times its weight of hot water, there is formed about equal quantities of camphoric anhydride and a new camphoric acid, which rotates the ray of polarised light to the *left*. These two bodies are contained in the precipitate after cooling, and form by far the bulk of the product. Besides these, there is formed a small quantity of another substance more soluble in water, which separates from a strong hot aqueous solution as an oil, after a time solidifying. This is a mixture of the ordinary dextro-camphoric acid with the new lævo-rotatory acid. I will refer to this again later.

The camphoric anhydride and lævo-camphoric acid obtained in this reaction are readily separated by treatment with carbonate of soda in the cold, by means of which the lævo-acid is dissolved, leaving the anhydride untouched. This anhydride is converted into the ordinary dextro-rotatory camphoric acid by solution in hot caustic soda and precipitation by hydrocbloric acid. I have been able to confirm de Montgolfier's observation that the camphoric acid obtained from the anhydride has a specific rotatory power of over +48°. I have found—

$$[\alpha]_D = +48{\cdot}25°.$$

(The determinations of rotatory power have been made throughout with a Laurent half-shade polarimeter, kindly lent me by Dr. Haldane, of the Physiological Department).

Properties of the Lævo-camphoric Acid.

The lævo-rotatory acid obtained above has a rotation about equal, and of opposite sign, to the dextro-acid. I have found $[\alpha]_D = -48{\cdot}69°$. I am convinced, however, that these two acids are not optically opposite isomers, in the sense namely in which dextro- and lævo-tartaric acids are regarded as optically opposite.

In its ordinary properties the lævo-acid differs markedly from the dextro-isomer. It has a lower melting-point, namely, 170° C., as compared with 185° C. Again it yields a very soluble amorphous barium salt, the corresponding salt of the dextro-acid being also indeed very soluble but crystalline. A more remarkable distinction, however, is that the lævo-acid appears to have no corresponding anhydride. When subjected to the action of acetyl chloride, an important reagent employed by Anschutz for obtaining the anhydrides of dibasic acids, the dextro-acid readily and practically quantitatively yields its anhydride, which is insoluble in carbonate of soda. The lævo-acid, on the other hand, when treated in the same manner, yields a product almost completely soluble in carbonate of soda, from which the original acid of melting-point 170° is recovered apparently unaltered.

Conversion of the Lævo- into the Dextro-Acid.

If, however, the lævo-acid be distilled, it boils about 294° C., yielding the anhydride of the ordinary dextro-camphoric acid, from which anhydride this acid may be obtained in the ordinary way.

Thus it appears possible to convert any quantity of the dextro-acid almost entirely into the lævo- through the intervention of the chloride, and any quantity of the lævo- back again to the dextro- by means of the anhydride.

Mixture of the two Acids.

Chautard obtained a lævo-camphoric acid by the oxidation of a lævo-rotatory camphor. This acid is described as possessing all the properties of ordinary camphoric acid, except that its rotatory power is of opposite sign. Further, when strong alcoholic solutions of the two acids are mixed, there is a precipitation of crystals and a rise of temperature in the liquid.

The lævo-acid which I have obtained differs from

* A Paper read before the Royal Society, December 5, 1889

Chautard's in other properties, and also in this, that when mixed with the dextro-acid in equal quantities in strong alcoholic solution there is no crystalline deposit and no rise of temperature.

On boiling down the alcoholic solution, a syrupy residue is left, which dissolves in hot water more readily, apparently, than either of its constituents. From the aqueous solution it separates partly as an oil, which after a time solidifies, and partly as crystals. Neither the solidified oil nor the crystals have a definite melting-point, but both melt at a lower temperature than either of the component acids. Hence the two acids do not appear to form any definite compound camphoric acid.

Separation of the Mixed Acids.

Anschutz's acetyl chloride reaction furnishes a particularly neat method of separating the two acids. The anhydride of the dextro-acid formed by the action of the acetyl chloride is separated from the apparently unaltered lævo-acid by treatment with carbonate of soda, which dissolves only the latter.

Nature of the more Soluble Syrupy Product of the Action of Water on Camphoryl Chloride.

This substance, which resembled the mixture of dextro- and lævo-acids above described, was subjected to the same process of separation, by which exactly the same products were obtained.

Thus the action of water on the acid chloride is such as to give about equal quantities of lævo-camphoric acid and the anhydride of dextro camphoric acid, a small portion of latter being further converted into the acid.

Optical Activity of Camphoryl Chloride and Camphoryl Anhydride.

It might be supposed, from the circumstances just mentioned, that camphoryl chloride which yields both dextro- and lævo-camphoric acids would be itself inactive. This, however, is not the case. I have always found camphoryl chloride to be lævo-rotatory, though I have not found a perfectly constant number to express its value. For the undiluted substance I have found $[\alpha]_D = -3{\cdot}0^\circ$ and $-3{\cdot}6^\circ$, while for the substance dissolved in crude benzene the rotation is about twice as much, viz. $[\alpha]_D = -7{\cdot}1^\circ$ and $-8{\cdot}3^\circ$; the latter value being obtained with the same specimen of camphoryl chloride which gave a rotation of $3{\cdot}6^\circ$ when undiluted. The rotation is, indeed, greater than that of camphoric anhydride, a substance which yields only one camphoric acid. I have found the specific rotation of camphoric anhydride in pure benzene to be $-3{\cdot}7^\circ$, and very little different in the same benzene which was employed for the camphoryl chloride.

De Montgolfier has given a higher value, $-7^\circ 7'$, for camphoric anhydride, which I am unable to confirm.

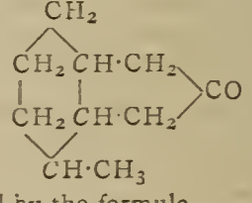
Theoretical Considerations.

If we wish to interpret rightly the foregoing facts, we shall, I think, find it impossible to regard the lævo-camphoric acid as the optically opposite isomer of the ordinary acid. On the other hand, there would appear to be a probability, almost amounting to certainty, that these two acids are related to one another as maleïc and fumaric acids, the dextro-camphoric acid corresponding to maleïc and the lævo- to fumaric acid. The isomerism is further complicated by the presence of rotatory power which requires the existence of two other isomers which shall be the optically opposite isomers of these two. In this latter case, therefore, the two acids will also be related, as maleïc and fumaric acid, but the lævo-acid will correspond to maleïc and the dextro- to fumaric. This lævo-camphoric acid is without doubt the acid which Chautard obtained by the oxidation of lævo-camphor, and the fumaroid dextro-acid I hope to obtain from it by the hydrolysis of the acid chloride.

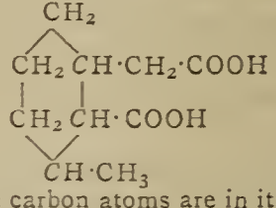
Now, accepting unreservedly Van't Hoff's carbon-atom hypothesis, we find that the isomerism of the camphoric acids is not explained by different structural formulæ, but ather by one and the same structural formula, admitting of at least four different arrangements of the atoms in space. There will be then two conditions attached to such a structural formula: (1) either it will contain two doubly-linked carbon atoms, each of them being united to two different groups, and one of these groups containing also an asymmetric carbon atom; (2) or the formula may consist of a closed chain of carbon atoms, of which two or more are asymmetric. In the latter case it is necessary to mention a further restriction, namely, that when there are only two asymmetric carbon atoms in the ring, there must not be symmetry in the formula, or, in other words, the image of neither isomer must be identical with its object (see *Phil. Mag.*, 1888, vol. xxvi., p. 426). It is the more necessary to mention this restriction as it applies to Wreden's formula, a formula which does not admit of rotatory power in the maleïnoid acid, that is, in the ordinary camphoric acid.

Turning now to some of the formulæ proposed for camphoric acid by different chemists, we find that in general they satisfy one or other of the conditions before mentioned. But Kekulé's formula, which fufils the first condition, and Kachler's, which satisfies the second, cannot be accepted, on the ground that they do not represent camphoric acid as a derivative of hexahydrometaxylene. Wreden's formula, which does thus represent camphoric acid, does not, as I have just mentioned, satisfy the restricted second condition. Armstrong's formulæ satisfy the second condition, and also represent camphoric acid as a derivative of hexahydrometaxylene; but Armstrong's formulæ appear to me liable to objection on the ground of the formula for camphor from which they are derived. These formulæ represent camphor either as not containing a ketonic group, or if it contains a ketonic group as containing also a closed chain of four carbon atoms. Now, we know no instances of stable rings of four carbon atoms, if indeed we know instances of such rings at all; and it is unlikely that camphor is the one exception to what may be regarded as a general rule.

The formulæ which I have proposed for camphor and camphoric acid appear to be opposed by no facts, and also explain perfectly the isomerism of the camphoric acids. Camphor is represented by the formula—

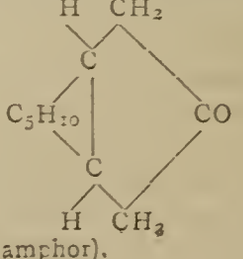


and camphoric acid by the formula—

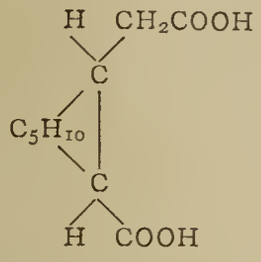


(The asymmetric carbon atoms are in italics).

Now the ordinary camphoric acid being the maleinoid acid has the two groups (COOH) and (CH_2·COOH) on the same side of the ring plane of the six carbon-atom nucleus. Hence in camphor, as we should naturally have supposed, the grouping $CO<\begin{matrix}CH_2—\\CH_2—\end{matrix}$ is also attached on one side of, and not across, the ring plane—

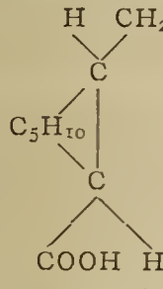


(dextro- and lævo-camphor).



(dextro- and lævo-ciscamphoric acid).

Again the lævo-fumaroid acid has the carboxyl and (CH_2COOH) groups on opposite sides of the ring plane.



(dextro- and lævo-transcamphoric acid).

On the other hand, Chautard's lævo-camphoric acid, being obtained directly from a lævo-camphor, will have the respective groups on the same side.

Nomenclature.

We may adopt the nomenclature introduced by von Baeyer to distinguish the hydroterephthalic acids. Ordinary camphoric acid, then, is dextro- and Chautard's acid lævo-ciscamphoric acid, the prefix *cis* indicating that the carboxylic groups are on the same side of the ring plane.

The new acid again, which I have described in this paper, is the lævo- and the acid yet to be discovered will be the dextro-transcamphoric acid, the prefix *trans* implying that the groups which govern the isomerism are on opposite sides of the ring plane.

It will be noticed that the formulæ which I have adopted require the existence of another series of two camphors (dextro- and lævo-) and four camphoric acids; but of the existence of these we have as yet no evidence.

Postscript, Dec. 2nd, 1889.—Since the above was written, my attention has been drawn to a paper by M. Friedel in the *Comptes Rendus* of last May, in which he describes a lævo-camphoric acid obtained from the substance known for some time as mesocamphoric acid. This lævo-acid appears to be the same as the one I have just described, and the mesocamphoric acid to be a mixture of the lævo- with the original dextro-acid. Thus mesocamphoric acid must no longer be regarded as a distinct isomer.

AN EASY METHOD OF DETECTING METALLIC SILVER IN THE PRESENCE OF LEAD.

By ALEXANDER JOHNSTONE, F.G.S. (Lond. and Paris),
Assistant to the Professor of Geology and Mineralogy in the University of Edinburgh.

As silver and lead very commonly occur in nature combined together in the same mineral substances, a more easy, rapid, and correct method for the detection of the former in the presence of the latter than any of those generally adopted in practice has for a long time been greatly desired, especially by assayers and mineralogists.

The author, who has spent much of his time in the determination of naturally occurring argentiferous lead compounds, has attempted to supply such a method in the extremely simple one detailed below, and he hopes it may prove, in the hands of others, as successful at it has invariably been with himself.

When a mineral which contains both of the above metals is heated in the ordinary course of blowpipe analysis, on charcoal with fusion mixture—

$$(K_2CO_3 + Na_2CO_3),$$

in the inner or reducing flame, it yields, as is well known, a malleable metallic lead (usually lead-grey in colour), which is an alloy of silver and lead. The silver is readily detected in this alloy* by treating it as follows:—Place it in an evaporating dish and cover it well over with moderately strong nitric acid, and then boil the liquid till the bead or beads dissolve; next nearly neutralise the solution thus obtained, with sodium carbonate, in a rough manner, but so that it will remain weakly acid after the operation. In this prepared solution now allow to lie for some time two strips—one of bright copper, and the other of zinc. The lead of the solution soon becomes deposited on the zinc, while the silver almost entirely goes to coat the copper foil; lift out the latter, and apply to the deposit on it a drop of fairly strong nitric acid, and then quickly afterwards a drop of potassium chromate solution. Or, dip the coated foil into moderately strong nitric acid for an instant, and then into a dish containing potassium chromate solution. The reddish brown mass which forms at once either on the upper or under side of the foil, is a sure indication of silver. The deposit on the zinc may be treated in the same way, and the lemon-yellow mass of lead chromate which results will contrast well with the brown incrustation obtained on the copper. If no silver is present in the solution the copper foil will scarcely become coated at all when placed in it.

LONDON WATER SUPPLY.

REPORT ON THE COMPOSITION AND QUALITY OF DAILY SAMPLES OF THE WATER SUPPLIED TO LONDON FOR THE MONTH ENDING NOVEMBER 30TH, 1889.

By WILLIAM CROOKES, F.R.S.;
WILLIAM ODLING, M.B., F.R.S., F.R.C.P.,
Professor of Chemistry at the University of Oxford;
and C. MEYMOTT TIDY, M.B., F.C.S., Barrister-at-Law,
Professor of Chemistry and of Forensic Medicine at the London Hospital; Medical Officer of Health for Islington.

To GENERAL A. DE COURCY SCOTT, R.A.,
Water Examiner, Metropolis Water Act, 1871.

London, December 9th, 1889.

SIR,—We submit herewith the results of our analyses of the 182 samples of water collected by us during the past month, at the several places and on the several days indicated, from the mains of the seven London Water Companies taking their supply from the Thames and Lea.

In Table I. we have recorded the analyses in detail of samples, one taken daily, from November 1st to November 30th inclusive. The purity of the water, in respect to organic matter, has been determined by the Oxygen and Combustion processes; and the results of our analyses by these methods are stated in Columns XIV. to XVIII.

We have recorded in Table II. the tint of the several samples of water, as determined by the colour-meter described in a previous report.

In Table III. we have recorded the oxygen required to oxidise the organic matter in all the samples submitted to analysis.

With one exception only, the whole of the 182 samples examined were found to be clear, bright, and well filtered.

The condition of the water supply to the Metropolis during the month of November has continued satisfactory; but, with the coming on of winter, there was noticeable,

* Silver, it will be remembered, is, in almost every case, present only as a *minute* constituent in lead ores.

as had been anticipated in a previous report, a slight increase in the small proportion of organic matter recorded as present in the water for now several months past. Thus the mean proportion of organic carbon in the water distributed by the five companies taking their supply from the Thames, which amounted to 0·138 part in September and to 0·143 part in October, was found to be 0·153 part in 100,000 parts of the water in November, with a maximum of 0·178 part in any single sample examined during the month. It is noticeable, moreover, that the mean proportions of organic carbon present in the New River and East London Companies' supplies, though below the actual mean present in the Thames-derived supply, yet exhibited a somewhat greater relative increase during the past month.

We are, Sir,
Your obedient Servants,
William Crookes.
William Odling.
C. Meymott Tidy.

DETERMINATION OF WATER IN SILICATES, SUCH AS TOURMALINE, VESUVIAN, MICA, &c.

By P. JANNASCH.

The author has worked out a method for effecting this determination when ferrous and ferric oxides, boric acid, and fluorine may be present. The author takes account of the circumstance that such minerals lose their water at very high temperatures, and simultaneously lose such volatile compounds as silicon- boron- and iron-fluorides.

The author opens them up by heating an intimate mixture of the silicate with lead chromate. Lead silicate is formed and all the water is set at liberty, whilst the halogens or other acid groups present remain in combination with the lead.

He uses thin tubes of potash glass of about 10—12 m.m. diameter within, and gives them the shape of a short combustion-tube of 46 to 47 c.m. in length. The previous ignition of the chromate, the drying, and filling the tube are effected in the manner usual in ultimate analysis.

The arrangement of the tube is as follows :—A current of air is introduced into a vacant space of about 4 c.m. at the end. Then follow copper turnings, 1 c.m.; granulated chromate, 10 c.m.; fine chromate, 1·5 c.m.; a mixture containing the substance, 6·5 to 7 c.m.; fine chromate, 5 c.m.; granulated chromate, 18 c.m.; copper turnings 1 to 2 c.m. Next follows an open space and then the perforated stopper.

The finely powdered mineral, dried previously for an hour over calcium chloride, must be intimately mixed with an excess of very finely ground chromate, so that the stratum of the mixture may take up a length of 6·5 to 7 c.m. in the tube. After the tube has been fully charged, and knocked so as to leave an air-channel, it is laid in a short combustion-furnace with about 20 round burners giving high flames. Before the calcium chloride tube is laid a soda-lime tube of the same shape, and in front of this a small U-shaped safety tube with fragments of potassa. The drawn-out end of the combustion-tube is then connected with a good drying system (potassa-lye, sulphuric acid, potassa in fragments, and granulated calcium chloride) and an air-gasholder. A slow current of anhydrous air—about 100 bubbles in a minute—is drawn through the apparatus and the heating is then begun and conducted much in the same manner as in a combustion. After the first layer is at full redness almost up to the substance and the end also, the remaining burners are opened almost simultaneously. The layer with the substance must be ignited as strongly as possible, as also the adjacent chromate, until it enters into fusion. After this heat has been attained it must be kept up for at least fifteen to thirty minutes, as strongly as possible.

Whilst the chief mass of the water collects in the calcium chloride tube the current of air is accelerated to about 150 bubbles per minute, though it is afterwards slackened again to the original rate. Both the drawn-out point and the front of the combustion-tube must project well out of the furnace. A movable screen at the front of the furnace is necessary. The foremost tile on the left of the current of air is omitted, and, where the substance lies, a tile is laid over the furnace. All the other tiles are placed close to each other. When the operation is complete the apparatus is not weighed before the lapse of an hour.—*Berichte Deutsch. Chem. Gesell.* and *Zeit. für Anal. Chemie.*

VOLUMETRIC DETERMINATION OF PHOSPHORIC ACID BY MEANS OF MOLYBDIC ACID.

By A. GRETE.

In the analysis of bone-dust in which the organic substance had not been entirely destroyed, the author observed that, after the addition of the first drops of the molybdic solution, there appeared a white flocky precipitate, which, on the further addition of the solution, seemed to become transformed into the ordinary yellow precipitate. The suspicion that the white precipitate was occasioned by the presence of gelatin was confirmed, as it was found possible to throw down all the phosphoric acid from a solution, on the addition of a sufficiency of glue, in the form of a flocculent precipitate, which, in more concentrated solutions, appears curdy. But all attempts failed to obtain, in this manner, in the cold, precipitates of a constant composition. The more glue was present, more was evidently taken up in the precipitate. In heat, also, the appearance of the precipitate varied according to the quantities of glue.

The author utilises these reactions as follows :—

A measured quantity of a solution containing phosphoric acid is neutralised in a beaker, using methyl-orange as indicator, and any slight turbidity is re-dissolved by a few drops of nitric acid. There is then added about an equal volume of a 75 per cent solution of ammonium nitrate, and about 1 grm. sodium sulphate and 1 c.c. of a solution of glue, heating to 80°—90°. The liquid thus prepared is directly titrated with a molybdic solution (prepared as below), agitating frequently until the clear liquid, after the addition of a drop, no longer shows any precipitation in the form of a dark cloud. The thick white precipitate produced at the beginning of the titration gradually becomes yellower and more curdy, so that further precipitations, which are white at first, show distinctly against this background. After shaking up the liquid it is tested again, adding, from time to time, small portions of glue as long as this alone produces any turbidity, and the approaching end of the operation is recognised by the decreasing strength of the reaction. When a precipitation can no longer be recognised on a drop of the standard molybdic liquid falling into the phosphoric solution, and when a solution of glue no logner produces a white turbidity, the whole (which should have been kept as hot as possible) is heated, whilst stirring, until the curdy precipitate becomes finely granular. In the clear liquid, especially if viewed from the side, the slightest turbidity occasioned by the further addition of a drop of the molybdic solution can be distinguished, and the liquid can then again be rendered clear by shaking.

If too much molybdic acid solution has been inadvertently added the error may be corrected by the introduction of a known number of c.c. of a solution of phosphoric acid and again bringing on the final reaction.

The presence of ammonium nitrate in increasing proportions depresses the results, which, however, can be kept constant if the above proportions are retained. On the other hand, sulphates slightly raise the results Varying quantities of acid act in the same manner, and should therefore be neutralised. But the acid which is introduced along with the molybdic solution does not interfere with the constancy of the results. Small quantities of chlorides have no appreciable influence upon the result.

The necessary solutions are prepared as follows :—

1. Molybdic acid solution :—1 kilo. ammonium molybdate dissolved in ammoniacal water and 100 grms. gelatin boiled for some time with water and a little nitric acid are mixed together, and the faintly alkaline yellow liquid is poured into about 3 litres of nitric acid of sp. gr. 1·2. The mixture is made up to 10 litres and kept for several days with frequent shaking. A flocculent phosphatic solution is soon deposited, after the removal of which the solution is perfectly clear and permanent, whilst without gelatin yellow deposits separate out.

2. Solution of ammonium nitrate at 75 per cent, containing about 40 grms. sodium sulphate per litre.

3. Solution of gelatin :—100 grms. gelatin are boiled in water and 50 c.c. nitric acid and made up to 1 litre. A few c.c. of this solution suffice for precipitating 0·1 grm. P_2O_5. If the gelatin solution contains phosphoric acid—which frequently happens—it must first be removed.—*Zeitschrift für Analyt. Chemie* and *Berichte Deutsch. Chem. Gesells.*

ON THE TANNIN IN INDIAN AND CEYLON TEAS.

By DAVID HOOPER, F.C.S., F.I.C.

The proximate constituents of tea leaves have been studied and estimated by various chemists with equally varying results and conclusions. The alkaloid therein, physiologically the stimulating principle of tea, has been determined in various samples, but the results have shown that no relation exists between the amount present and the commercial value of the leaf, or the elevation at which the bushes grow. A number of elaborate analyses have been published on the composition of the inorganic matter or ash of tea, but it seems that no useful lessons to the planters can be drawn from these tables.

The tannin of tea has also been investigated, both qualitatively and quantitatively, but as the subject has been treated by so many experts, using different methods, and applying them to different samples, the results are not comparable, and leave the subject open for further enquiry.

Mulder's analyses of tannin in teas are often quoted in text-books; his figures for black tea are 12·88, and green tea 17·80 per cent; Dragendorff found in teas of Russian commerce 9·42 to 12·70 per cent; Jank obtained a maximum of 9·14, and a minimum of 6·92 per cent in eighteen samples; Wigner, analysing some astringent teas, reported as much as 27·7 to 42·3 per cent; Hassell gives as the average 15·24 in black, and 18·69 per cent in green teas; Clark found from 5 to 19 per cent; and Geisler, an American chemist, obtained 14·87 as the average percentage of tannin in a large number of packages of Indian teas imported into New York.

The interpretation of these figures has been also remarkable. Some isolated analyses have recently gone the round of the Indian papers, to the effect that an Indian tea gave 9·68 per cent of tannin, and a Chinese tea 6·01 per cent, and these figures have been quoted with a view to disparage Indian teas, and to exalt the virtues of Chinese leaves. The teas of Ceylon have also been examined, and from a few analyses it has gone forth that the tannin, as a rule, in the teas of this island

	Description of sample.		Elevation.	Tannin Per cent
Nilgiris—				
1.	Dodabelta, Orange Pekoe ..		7800	13·55
2.	,, Pekoe		,,	13·23
3.	,, Souchong		,,	12·32
4.	,, Congou		,,	11·08
5.	Green leaves, inferior		7000	19·19
6.	,, Liddellsdale ..		6500	16·38
7.	,, Young bushes ..		,,	19·00
8.	,, Hybrid		6000	18·66
9.	,, China variety ..		,,	16·62
10.	,, Assam hybrid ..		3100	21·03
11.	,, Coarse..		,,	11·52
12.	Hope Estates, Orange tips ..		4000	18·61
13.	,, Orange Pekoe ..		,,	18·35
14.	,, Broken Pekoe ..		,,	17·52
15.	,, Pekoe		,,	16·85
16.	,, Pekoe Souchong		,,	17·53
17.	,, Souchong.. ..		,,	15·88
18.	,, Congou		,,	13·19
19.	,, Tray dust.. ..		,,	18·55
20.	,, Bulk tea		,,	18·00
21.	,, Green	Mandarin broken	,,	24·37
22.	,, Green	,, Pekoe	,,	23·85
23.	,, Green	Bulk	,,	23·50
24.	Aratapara, Orange Pekoe.. ..		3400	14·48
25.	,, Pekoe		,,	14·14
26.	,, Pekoe Souchong ..		,,	12·25
27.	,, Souchong..		,,	11·96
28.	,, Congou		,,	10·14
29.	,, Dust..		,,	14·42
Travancore—				
30.	Seafield, Broken Pekoe		2500	19·95
31.	,, ,, ,, ...		,,	21·22
32.	,, Pekoe Souchong ..		,,	20·90
33.	,, ,, ,, ...		,,	21·13
34.	Poonmuddi, Broken Pekoe ..		2600	17·45
35.	,, Pekoe		,,	17·37
Coorg—				
36.	Munza-collie, Orange Pekoe ..		4000	16·93
37.	,, Pekoe		,,	16·32
38.	,, Souchong		,,	15·15
Ceylon—				
39.	Glenorchy, Broken Pekoe ..		5700	19·00
40.	,, Pekoe		,,	17·90
41.	Brownlow, Broken Pekoe.. ..		4000	20·80
42.	,, Pekoe		,,	19·22
43.	Ancombra, Broken Pekoe.. ..		2500	18·40
44.	Yellangowry, Pekoe		,,	15·67
45.	,, Pekoe Souchong .		,,	15·00
46.	Bandarapolla, Broken Pekoe ..		1600	18·53
47.	,, Pekoe..		,,	17·40
48.	,, Pekoe Souchong		,,	17·20
49.	Kanangama, Broken Pekoe ..		200	20·87
50.	,, Pekoe		,,	17·48
51.	,, Pekoe Souchong .		,,	15·41
Assam—				
52.	Orange Pekoe		600	20·80
53.	Pekoe		,,	20·43
54.	,, ...		,,	18·68
55.	,, ...		,,	19·25
56.	Broken Pekoe Souchong.. ..		,,	16·83
57.	Pekoe Souchong		,,	16·18
Darjeeling—				
58.	Orange Pekoe		3000	13·61
59.	Broken Pekoe		,,	17·74
60.	Pekoe		,,	16·37
61.	,, ...		,,	13·67
62.	Pekoe Souchong..		,,	14·74
63.	,, ,, ...		,,	14·64
64.	,, ,, ...		,,	14·52
65.	Fannings		,,	15·25

is much smaller than in Indian specimens. Again, tea growers on the mountain tops have used figures to show the superiority of their produce compared with that of the plains, and the following extract taken from a local paper, circulating in a planting community, will show what ignorance is displayed on the subject :—

"The strong rasping Assam brew, and the make of all gardens situated at low elevations, are known to contain upwards of 75 per cent of tannin, while mountain trees are comparatively free from this deleterious ingredient."

The tannin of tea leaves, according to Rochleder, Hlasiwetz, and Malin, is allied to quercitannic acid, and according to Kellner is identical with gallotannic acid. It is precipitated from its solution with acetate of lead, forms an insoluble precipitate with gelatin, and inky mixtures with salts of iron ; it is associated with gallic acid, boheic acid, oxalic acid, and quercetin, and is the source of the astringency of the tea. From the numerous methods for the estimation of tannin, the one that commended itself to me was the use of a solution of acetate of lead to a filtered decoction containing by exhaustive boiling the soluble constituents of the leaves. The process is simple, and it was found to give most concordant results when working on the same sample. The lead precipitate would contain some of the gallic acid and the oxalic acid, if any were present, and therefore the weight of this precipitate was an excellent gauge of the astringent properties present; the dried precipitates were found to have a composition averaging 50 per cent of plumbic oxide, a result agreeing with the constitution of gallotannic acid. The value of the present investigation consists in the observance of the minutest detail in the process being carried out under exactly similar conditions, although applied to different samples. The teas were all air dried, and contained from 5 to 6 per cent of moisture, the green leaves were dried in a water-oven previous to analysis, and the results were calculated upon the leaves containing 5 per cent of moisture.

It will be observed in the above Table that the finest teas are those which contain the most tannin, and there is a gradual declension of this principle as we approach the Souchong and congous. The elevation does not appear to affect the amount of tannin as has been supposed. The Dodabelta Estate, the highest in the list, shows a smaller percentage of tannin in the leaf than all the rest, but does not very much differ from the samples from Aratapara, some 4400 feet below; and in this respect there is very little to learn from the altitudes of the Ceylon teas. The highest tannin content occurs in Travancore tea of Seafield Estate, a tea of great fragrance, and considered to rank very high-class in the home market, and the Glenorchy Broken Pekoe of Ceylon, although containing 19 per cent of tannin, is one of the best priced teas of the island. The determination of Nos. 9 and 10 shows that the kind of shrub cultivated in India contains more or less tannin according to its original habitat. The coarse leaves, No. 11, were taken from the lower part of the bush, and were such as are never made use of in the factory. The green teas are very astringent, and, as they are made from the same estate as those above, it is evident that some of the astringency is rendered insoluble in the process of manufacture.

The amounts of tannin shown in the list, it must be remembered, are obtained by perfectly exhausting the leaves, and do not represent the amount taken in domestic use. The infusion of the family tea-pot extracts more or less tannin, according to the sample used and the time allowed for the leaves to soak in the boiling water. The brokers' test of five minutes takes out one-fifth of the extract, with a corresponding amount of tannin. The tea-pot infusion of ten minutes removes about one-third, fifteen minutes one-half, and twenty minutes two-thirds. The following experiments were made to show the amount extracted by infusing 1 per cent of tea in boiling water for five and fifteen minutes :—

	Tannin. Per cent.	Extracted in five minutes. Per cent.		Extracted in fifteen minutes. Per cent.	
A. ..	11·08	3·04	27·4	—	—
B. ..	12·10	4·40	36·2	6·88	56·8
C. ..	12·32	4·28	34·7	—	—
D. ..	13·25	—	—	7·88	59·5
E. ..	13·55	4·60	33·9	—	—
F. ..	23·50	6·26	26·6	9·52	40·0

The tannin is, undoubtedly, the source of the "strength" of the tea, and the higher the tannin the richer the infusion, and the more of body will the sample possess. Tannin is likewise a natural constituent of the tea, and is not amenable to suppression by higher cultivation, or by the ordinary processes of manufacture. The excellent qualities of Indian teas are accompanied by a high percentage of this substance, and therefore must be treated as strong teas, either by diluting them with weaker Chinese, or by taking a much smaller quantity when required for infusion in the tea-pot. If a smaller amount of these strong teas is taken, if good water is used for the infusion, if it is allowed to stand not longer than ten minutes, we should not hear so much of the "deleterious ingredient" in this universally used beverage.

Ootacamund, India.

THE MAGNETISM OF NICKEL AND TUNGSTEN ALLOYS.*

By JOHN TROWBRIDGE and SAMUEL SHELDON.

Introductory.

The fact that different kinds of steel, alloyed in small proportions with tungsten or wolfram, and magnetised to saturation, increases in specific magnetism,† has long been known. Whether the same effect would result from the use of nickel alloyed with tungsten has never been investigated. This paper has for its object a partial answer to the query. It was instigated by Mr. Wharton, proprietor of the American Nickel Works, whose chemist, Mr. Riddle, kindly prepared the alloys which have been employed. These alloys were in two groups. The first, received in November, 1888, consisted of three bars of the same shape, one being of pure nickel and the other two having respectively 3 and 4 per cent of tungsten in alloy. These bars were rolled from cast ingots, which were toughened by the addition of magnesium after Fleitmann's method, the magnesium being added just before pouring. They were hot when rolled. The one of pure nickel was afterwards planed into regular shape. Those containing tungsten were too brittle to allow of this manipulation. They were, however, of sufficient regularity to permit accurate measurements. This group contained also an octagonally-shaped bar with 8 per cent of tungsten, which was prepared like the others, and was afterwards ground into shape.

The second group, received in May, 1889, contained bars which were simple castings, made without the addition of magnesium, and consisted of pure nickel and alloys with 1, 2, 3, and 6 per cent of tungsten. All the bars in this group were extremely hard and brittle. In making them, tungsten oxide, of weight calculated to yield the desired percentage of tungsten in the resulting alloy, was placed with adequate carbon in the bottom of a graphite crucible and covered by the proper weight of pure grain nickel. All was then covered with borax, the lid of the crucible was placed on, and the crucible was heated until reduction and fusion were completed.

* From the *Proceedings of the American Academy of Arts and Sciences.*

† *Journ. Chem. Soc.*, 1868, xxi., 284, says 300 per cent

Method.

As the suspected influence of the tungsten would be to affect the magnetic moment of the bars, these were magnetised to saturation and their specific magnetism then determined, *i.e.*, the magnetic moment for each grm. of metal.

The magnetisation was effected by placing the bars separately in a hollow coil whose length was 15 c.m. and outside and inside diameters respectively 6 and 3 c.m. It consisted of six layers of wire having 63 turns each. A dynamo current of 40 ampères was then sent through the coil for one minute, and the circuit then broken and the bars removed.

For the determination of the magnetic moment, use was made of a reflecting magnetometer, and deflections were observed with a telescope and scale at a scale-distance of 100 c.m. Measurements of the horizontal intensity, H, of the earth's magnetism were first made. The results from these determinations by means of the first and second Gauss arrangements were, respectively,—

$$H = 0{\cdot}1724 \text{ c.m. g. s.}$$
$$H = 0{\cdot}1720 \quad ,,$$

The freshly magnetised bars were then placed in the second Gauss position relative to the magnetometer, and the angular deflection determined. The specific magnetism, S, was then calculated by the formula—

$$S = \frac{r^3 H \tan \phi}{m},$$

where—

r = Distance from bar to magnetometer = 72·68 c.m.
H = Earth's horizontal intensity = 0·1722.
m = Mass of the bar.
ϕ = Angular deflection of magnetometer.

Results.

The mean results of two sets of observations on Group I., and also upon a similar bar of soft tool steel, are given in the following Table :—

Group I.

Composition.	Size in c.ms.	Mass in grms.	S[c.m. $\frac{5}{2}$ g.$-\frac{1}{2}$ sec.$^{-1}$]
Pure nickel	18×2·7×0·65	284·5	1·23
Ni+3 p.c. W	,, ,, ,,	286·5	10·60
Ni+4 ,, W	,, ,, ,,	283·5	10·40
Tool steel	15×2·5×0·5	159·5	7·46
Ni+8 p.c. W	(13×1·5) (octagonal)	144·0	5·25

roup II., of cast bars, gave the following results :—

Group II.

Composition.	Size in c.ms.	Mass in grms.	S[c.m. $\frac{5}{2}$ g.$-\frac{1}{2}$ sec.$^{-1}$].
Pure nickel	18×1·8×1·6	459	1·05
Ni+1 p.c. W	,, ,, ,,	455	1·92
Ni+2 ,, W	,, ,, ,,	454	1·70
Ni+3 ,, W	,, ,, ,,	463	1·75
Ni+6 ,, W	,, ,, ,,	465	1·15

The bars of both groups were, subsequent to the above observations, completely demagnetised and then freshly magnetised. New determinations gave the same results as before. The demagnetisation was accomplished by placing the bars inside two coils, which were traversed by currents from an alternating dynamo. The coils were then slowly drawn apart, and the bars maintained at a position central between them. After treatment in this manner, they showed no appreciable deflection when placed in position relative to the magnetometer.

The results tabulated indicate that tungsten greatly increases the magnetic moment of nickel, if the alloy be forged and rolled, but, on the other hand, has but small influence if they be simply cast. Furthermore, changes in the amount of tungsten do not appear to cause corresponding changes in the magnetic properties.

To see whether the remarkable effect in bars 2 and 3, as compared with bar 1, of Group I., was owing to some molecular condition of their surfaces induced by rolling, two bars from the same steel, one rolled and the other pressed, were magnetised and then measured. The ratio of the specific magnetism of pressed to rolled was 9 to 5, the rolled having the smaller amount. The existing difference, in this case, is probably owing to a difference in hardness, rather than to any molecular condition of the surfaces.

The specific magnetisms of all the bars are small when compared with good steel magnets. Kohlrausch says that good magnets, of common form, should have S=40. The bar of ordinary tool steel, however, retained but 7·46. Still it was soft, and by tempering would doubtless have doubled this value.

If forged, nickel and tungsten can be made to maintain a specific magnetism of 10; it will form a useful addition to the resources of physical laboratories. From the high polish of which it is susceptible and its freedom from damaging atmospheric influences, it will be most happily suited for the manufacture of mirror magnets where magnetic damping is to be employed.

CONTRIBUTION TO THE KNOWLEDGE OF BORON.*

By HENRY C. C. MAISCH, Ph.G., Ph.D.

During his researches on the electrolysis of the alkaline oxides and hydroxides, Sir H. Davy also subjected boric acid to the action of the electric current (*Phil. Trans. Royal Society*, 1808, p. 43). He obtained a black combustible substance, which, however, he did not further describe. Without doubt he was the first to obtain boron in the free state, though to two French chemists, Gay-Lussac and Thénard (*Gilb. Ann. der Phys.*, 1808, p. 30), belongs the credit of first describing the element, which they obtained by the action of potassium on melted boric acid. During the year 1888, W. Hampe (*Chem. Zeit.*, xii., 841) prepared boron by the electrolysis of borax, which he melted in a graphite crucible.

Wöhler and Deville (*Ann. Chim. Phys.*, 1858 (3), lii., p. 84) during their classic researches on boron and its compounds, employed the process of Gay-Lussac and Thénard, using potassium or sodium, but they also found that, by using aluminium, crystalline boron was obtained.

We are indebted to Berzelius for two further methods: (1) by the action of potassium on boron fluoride, and (2) by the action of potassium borofluoride at the fusing-point of the former. Wohler and Deville (*loc. cit.*) and Geuther (*Jenaische Zeitschr. fur Med. und Naturw.*, ii., p. 209) found that, in place of potassium or sodium, magnesium could be used to advantage in the last method.

On the advice of Prof. L. Gattermann I took up the reduction by means of magnesium, using, in place of potassium borofluoride, the cheaper borax. This was employed in the form of powdered borax glass, because the water of crystallisation otherwise present would have an injurious effect on the reaction.

Without going into details as to the experiments made with the idea of finding the best proportion of the reagents to be used, I will simply give the one which was found to be the best. The bottom of a Hessian crucible was covered with the powdered borax glass; on this an intimate mixture of two parts borax and one part magnesium powder was packed, so as to drive out as much air as possible, and this was covered by about half an inch of powdered borax glass, which is to fill the crucible. The lid is then fastened down with moist clay, and the whole

* *Am. Journ. Pharm.*, December, 1889.

subjected to the heat of a well-drawing charcoal furnace, the crucible being surrounded by the fuel, which is allowed to burn down once. After cooling, the crucible is broken and the product finely pulverised. The powder is extracted with, boiling water, and, after cooling, thrown in small portions into cooled diluted hydrochloric acid and allowed to remain for four or five hours, after which it is filtered off and subjected to the action of concentrated hydrochloric acid for about two hours. The powder is then filtered off, washed with water, and dried either by the heat of a water-bath or by the following method:—The water is replaced with alcohol, this in turn by ether, and this allowed to evaporate at the temperature of the room. The boron thus obtained is by no means pure, but answers perfectly well for the preparation of its halogen derivatives.

Boron Trichloride.—The first method to be found in literature is that of Berzelius (*Pogg. Ann.*, 1824, ii., p. 147), who states that amorphous boron which has been dried in a vacuum ignites in an atmosphere of chlorine at ordinary temperatures, while boron which has been heated reacts only at higher temperatures. Some decades later Wöhler and Deville (*loc. cit.*) showed that the same takes place in hydrochloric acid gas; the reaction, however, must be completed at higher temperatures. They also found that by the action of boron on mercuric chloride, lead chloride, or silver chloride, this compound was likewise obtained.

The method which has been used up to the present for the preparation of the chloride is that of Dumas (*Ann. Chim. Phys.*, 1826, xxxi., p. 466; xxxiii., 376), who allowed chlorine to pass in a tube over a heated mixture of powdered melted boric acid and charcoal.

It seemed to be of interest to ascertain how the boron prepared by the above method would behave towards chlorine. The apparatus which was used was the following:—A hard glass tube, as used for combustions, about 4 to 8 inches longer than the combustion-furnace to be used, is drawn out at one end and bent almost at right angles. This part is attached to a Peligot's tube, which is surrounded by a freezing mixture of ice and salt. All the necessary joints are made by means of smooth and closely-fitted corks. The air-dry boron is loosely spread in a combustion-tube, so that it is one-fourth inch in thickness all through; and as the boron must be thoroughly dry the water is driven out by heating in a stream of hydrogen, also allowing it to cool in the same. Carbonic acid cannot be used, as boron reduces it completely to carbon monoxide, as noticed by Lorenz (*Ann. Chem.*, 1889, ccxlvii., p. 226). After the tube has cooled the hydrogen is forced out by a stream of dry air, and the larger end of the tube then connected with a chlorine generator. The chlorine is prepared from manganese dioxide and hydrochloric acid, and best regulated so that a slow but steady stream is obtained. The whole apparatus is filled with washed and dried chlorine gas before heat is applied, sufficient for producing a slight glow in the tube. A liquid having the colour of chlorine gas condenses in the Peligot's tube, which is best connected with a good drawing chimney, as some of the trichloride goes through uncondensed. The colour of the liquid is due to dissolved chlorine, which is removed by shaking the liquid with mercury in a sealed tube, which can also be used for distilling. After the liquid has become perfectly colourless, which takes about two days, the tube is opened, and, by means of a closely-fitting cork, a narrow glass tube, twice bent at right angles, is attached. The one arm of the tube which is used as a condenser is to be about 20 inches long, and projects to the bottom of the receiving vessel, which is surrounded by a freezing mixture of ice and salt. The best receiver is a wide glass tube about 25 inches long and about 5 inches below the orifice drawn out, so that the condensing tube just moves freely in the opening. The distillation is best carried on by means of warm water, very slowly, so as not to lose too much of the chloride—this boiling at 18° C. The yield of the chloride by this process is as follows:—By using 8 grms. of magnesium powder for reduction the boron gave 15 grms. of the chloride, the theoretical yield being 26 grms.

NOTICES OF BOOKS.

A Handbook of Modern Explosives: being a Practical Treatise on the Manufacture and Application of Dynamite, Gun-cotton, Nitroglycerin, and other Explosive Compounds, Including the Manufacture of Collodion-Cotton. By M. Eissler, Mining Engineer and Metallurgical Chemist. London: Crosby Lockwood and Son.

The author of this work published sbout five years ago, in New York, a treatise on "The Modern High Explosives."

The book now before us, though very similar in its general character, is drawn up with more reference to the demands of a British public, containing, as it does, an abstract of the Explosives Act now in force in this country, the instructions, issued under the authority of the Home Office, for determining the stability of explosives, and the forms of application for authority to manufacture or import any new explosive. The work also contains the processes of Captain Hess for the analysis of explosives. Here we notice, as far as gun-cotton is concerned, some decided improvements as compared with earlier practice. Thus, in determining the mineral matter, the sample is first impregnated with paraffin, upon which it burns away quietly, without any projection or loss of the ash.

The separation of trinitrocellulose from cotton fibres which have escaped nitration is effected by taking a portion of the gun-cotton, after the mono- and dinitrocellulose have been dissolved out in the usual manner with absolute alcohol and ether, and repeatedly boiling in an excess of a saturated solution of sodium sulphate; any raw cotton existing in the sample remains undissolved in company with the insoluble mineral matter.

The author, however, points out, on the authority of Böckman, that neither gun-cotton, collodion-cotton, nor nitro-glycerin can be viewed as true nitro-compound, as, for instance, is picric acid. They are rather to be regarded as ethers of nitric acid.

Concerning melinite, we find some more definite information than has yet been discovered. It has generally been described as a mixture (or compound) of which picric acid is merely one of the ingredients. Here, however, melinite is said to consist simply of picric acid compressed and then either agglomerated with an aqueous solution of gum arabic or a fatty body, or cast by fusion at 130° to 145° and poured into the moulds. The discovery is announced that picric acid alone, such as it is found in commerce, "is one of the most powerful explosives that can be conceived; its explosive force is greater than that of compressed gun-cotton and the different forms of dynamite, whilst its insensibility to shock, as well as its stability, are very remarkable."

He demonstrates that "the maximum force of this kind, contrary to what has been believed, does not coincide with the chemical formulæ which corresponds to complete combustion, but, on the contrary, with the combustion which yields carbonic oxide."

The advantages claimed for picric acid, especially for military uses, are:—Absolute chemical stability, *i.e.*, non-susceptibility to spontaneous decomposition or elementary change; absolute physical stability, *i.e.*, non-liability to congelation, exudation, liquefaction, or evaporation; it is non-hygroscopic, insensible to the most extreme variations of natural temperature; free from danger in manufacture, manipulation, and transport; and insensible

(in shells) to the shock of the discharge of cannon. We are told that a substance called "Lydite," much resembling melinite, is under examination by our Government.

The subject matter of this work has its painful sides. The author speaks of the "great benefits which have been conferred upon the world at large by the invention of these explosives," and he expresses the hope that they may find their "exclusive employment" in the operations of the civil and mining engineer.

We cannot, however, help expressing the fear that such inventions have occasioned, and may yet occasion, more harm than good. Without dynamite the "dynamitard" could not have existed. Since, however, these compounds have come into existence, no nation can afford to ignore them, and hence Mr. Eissler's work is of unquestionable value.

Electrical Distribution of Heat, Light, and Power. By Harold P. Brown, Electrical Engineer. With a partial List of Deaths from Electrical Lighting Apparatus, with an Address by John Murray Mitchell, Counsellor-at-Law, on Legislative Control of Dangerous Electrical Currents. New York: J. W. Pratt and Son.

This pamphlet consists essentially of an address delivered by the author on June 4th last, before the International Medico-Legal Congress. Its object is essentially a protest against the use of alternating currents, especially if at high tensions, and, as far as we can judge, most of all against the Westinghouse system. He contends that burying the wires is no protection. Yet, we must say, after carefully reading over the list of fatalities, some of them never could have happened if the wires had been laid underground. These men were killed "by touching telegraph wire *hanging* over Westinghouse circuit," by "trailing alternating current wire," by "touching dangling telegraph wire," "touching hanging telegraph wire," "touching dangling telegraph wire." We submit that there ought not to be any trailing, hanging, or dangling wires.

Upon experts, or "professional scientists," Mr. Brown is very severe. He writes that a representative of this class believes that "his opinion must necessarily coincide with the wishes of the corporation which retains him, no matter if scientific accuracy must be sacrificed." Again, he tells us that "when the water-gas question was under discussion some years ago, one of this fraternity gave his written opinion to a New York gas syndicate that a small percentage of carbonic oxide in illuminating gas was necessarily fatal. Shortly after, he was 'acquired' by a water-gas system, and testified without hesitation that 32 per cent of carbonic oxide need not be regarded as detrimental." If such misrepresentation of science exists, in New York or elsewhere, the fact is greatly to be deplored and protested against.

May we, without touching too strongly national susceptibilities, remark that recklessness in matters concerning the public safety is more strongly manifested in America than in Britain? Precautions, if costly, are more generally neglected, and such neglect on the part of a wealthy and influential company is either condoned or there is a difficulty in bringing the offenders to justice.

It by no means follows that if high tension alternating currents are introduced among us that they will occasion such accidents as Mr. Harold Brown enumerates.

On the Ventilation of Schools: a Lecture delivered before the College of State Medicine, May 22nd, 1889. By Sir Henry E. Roscoe, M.P., F.R.S., D.C.L., LL.D. London: T. W. Danks and Co.

The publication of th s lecture may be called very timely, in view of the recent disclosures concerning the sanitary, or rather unsanitary, condition of not a few primary schools. A glance at its date, however, will show that it was not written with any reference to the late revelations. On the contrary, the author seems to be of opinion that Board Schools, in the matter of ventilation at least, are in a better condition than those establishments to which he applies the offensive name of "private *adventure* schools," a term invented by school board authorities. His enquiries do not, it seems, extend to boarding schools, where, we suspect, the results, if procurable, would not be reassuring.

Among the important points brought to light is the fallacy of the routine assumption that the atmosphere of the upper part of a dwelling room, above the level of the chimney-piece, was richer in carbonic acid than the lower part. This view was plausible, but it does not stand the test of actual analysis.

The table of the volumes of carbonic acid contained in 10,000 vols. of air in different localities will be likewise a revelation to many readers; whilst the normal proportion is given as four. That of the Madrid hospitals ranges from 27 to 43; that of the London theatres 8·2 to 32; and that of mines to 78·5. It will also be a surprise that the average for London, 4·4, exceeds that of Manchester, 4, whilst in the Metropolitan tunnels the proportion is 14·5.

Sir H. Roscoe shows likewise the fallacy of the supposition that the amount of carbonic acid in any given locality varies as the organic matter. This is proved, *inter alia*, by the fact here mentioned, that "during a course of crowded popular lectures in the new lecture theatre of University College, Dundee, an average of only four microbia per litre was found, as compared with an average of about 3 when the room had remained empty. Nor did the average rise beyond 6 per litre when the room was left unventilated during the lecture, whilst the carbonic acid rose to nearly 40 vols. per 10,000.

It is shown that a mere determination of readily oxidisable matter in a given volume of air is not sufficient, since the various methods proposed for this purpose fail to distinguish septic or pathogenic matter from that which is relatively harmless. Hence, in all comparative examinations of the air of different localities the bacteriological methods of Pasteur, Koch, and Klein have to be brought into play. Here we come upon the startling fact that in a "naturally ventilated" school at Dundee the number of bacteria in 18 litres of air reached 1510, whilst in the bed-rooms of the one-room houses of the same town, the proportion was only 585, a number, of course, far too high, but small in comparison with that in the schools.

The origin of the microbia in the air of houses and schools is still undecided. They are not given off to any appreciable extent in the ordinary respiration of healthy persons. Neither does the floor, with the loose dirt lying about on it, appear to be at fault. Scrubbing the floor does not appear to have any permanent effect in diminishing the microbia. Thus, two similar school-rooms were taken: one was scrubbed once a week for five weeks, and the other was left unscrubbed. The total effect of the scrubbing was nil. Other things being equal, there are fewer bacteria in the air on damp or still days than on dry or windy days.

The author is of opinion that enlarged air-room per head and improved ventilation in primary schools would "pay" our educational authorities. Into this question the Chemical News cannot enter, though we may remark that the money which has been expended on board schools, if it had been honestly and judiciously laid out, would have been amply sufficient for the improvements which Sir H. Roscoe and Dr. Carnelley recommend.

Seventh Annual Report of the Board of Control of the New York Agricultural Experimental Station for the Year 1888. Albany: Troy Press Company.

From the Report of the Executive Committee it would seem that the Station, prior to its purchase by the State, had been allowed to fall into a state of ruin and neglect.

According to the Treasurer's Report the Laboratory cannot be accused of extravagance, its outgoings for the past twelve months not exceeding the modest sum of 25¾ dollars.

A startling piece of information is that eggs are imported *into* the United States on a vast scale, the total for 1885—the last year given—being 16 million dozens. Whence they came we do not learn.

Trials have been made at the station with various compounds as insectides. The chemicals used were "Paris green," a copper arsenite, "London purple," a residue from the manufacture of magenta by the Medlock process, and the "Zoëktein" poison. The substance bearing this alarming name is an arsenical compound of unknown composition.

For the "codling-moth" (*Carpocapsa pomonella*), Paris green proved the best remedy.

The "cabbage maggot" was attacked with salt water, with McDougall's sheep dip, diluted with 5 parts of water, with Zoëktein, and with kerosene. The brine had no effect; the sheep-dip did not harm the insects, but was fatal to the plants, whilst Zoëktein and kerosene destroyed both.

Sodium thiosulphite and potassium sulphide proved useful against parasitic fungi. Calcium sulphide, on the contrary, was found of doubtful value.

The trials with manurial matters led to the adoption of 17½ cents per lb. as the value of ammoniacal nitrogen; 16 as that of nitric nitrogen. Organic nitrogen ranges from 16½ in dried ground fish, blood, and cotton-seed, to 8 in horn-shavings and hair. Phosphoric acid, soluble in water or in ammonium citrate, is valued at 8 cents per lb., but that in finely ground mineral phosphate only at 2. Basic slag does not seem to have been tried.

The sale of manures in many of the States is subject either to a license, which may reach 500 dollars, or in others to a fee for analysis by the State agricultural chemist.

Manual of Assaying Gold, Silver, Copper, and Lead Ores With One Coloured Plates and Ninety-four Illustrations on Wood. By Walter Lee Brown, B.Sc. Third Edition. Chicago: E. H. Sargent and Co.

The author takes exception to existing treatises on assaying, either as antiquated in their methods and apparatus, or as being more books of reference than manuals.

Mr. Brown begins with a description of the apparatus used in assaying. It might, perhaps, be said that figures of balances and weights are scarcely necessary in these days. The explanation of the "assay-ton" is very clear and is given both to suit the metric system, the American ton (2000), and the British ton of 2240 lbs.

He describes a furnace which he has constructed and named the "Monitor," but which he recognises as an application of a principle due to Mr. Fletcher, of Warrington. As for crucibles and muffles, he recommends those of the Morgan Crucible Co., Battersea.

Among the apparatus mentioned is a "casserole," which is a deep porcelain capsule or crucible fitted with a handle.

In the list of reagents and the remarks as to the examination of their purity we find nothing calling for remark.

In the section of the book which treats of the practical operations of assaying, the author remarks that the colours shown by the interiors of scorifiers are often characteristic of the ores operated upon, and, in conjunction with the colours of the cupels after cupellation, make valuable tests. Of these he describes and figures very beautifully the colours given by ores containing uranium, chrome, manganese, copper, iron, and lead. Under lead he remarks that vanadium, cadmium, and bismuth give the same shades. The colours given by nickel and tellurium he does not consider very characteristic.

The instructions for the assay of gold and silver ores are fully on a level with the practice of the day, every operation being fully and clearly described.

Concerning the assays of copper and lead by the dry way, he admits their inaccuracy, and recognises that, especially as far as copper is concerned, they are being everywhere superseded by the more exact volumetric and electrolytic methods, which, accordingly, he describes in the appendix.

We must, however, take exception to the following passage:—"In a certain sense no one cares to know the ultimate amount of metal that an ore contains. What is desired in practice is the *yield* under the most skilful treatment, and this information is approximately obtained by fire for copper."

Now an intelligent metallurgist wishes to know the exact amount of metal in his ores that he may see how near his working processes come to perfection. The dry assay—Cornish at least—shows *less* copper than can be obtained on the large scale, in a proportion which is the greater the poorer the ore, and, according to the vicious system of the English copper trade, this excess over and above the results of the assay is the smelter's profit.

The appendix also contains lists of the principal gold and silver minerals found in the United States, as also of those which may prove auriferous or argentiferous. We venture to suggest that a similar catalogue for Australasia and South Africa would prove very valuable if carefully compiled. We cannot do other than recommend this book as valuable and trustworthy.

Introductory Lessons on Quantitative Analysis, suitable for the Examinations of the Science and Art Department and the University of London. By John Mills and Barker North.

The work before us is purely an outcome of our vicious system of secondary education. There is nothing in it, however accurate, which cannot be found again and again in other accessible works. We are therefore compelled to ask, as in case of the majority of chemical manuals issued, *cui bono?* The authors are, in their teachings, avowedly examinational. They write for "students in evening classes who have but little time to spare in acquiring such knowledge." Now, to assist people in "passing" who have not time to "know" is an aim which we cannot applaud, and the existence of such a class of persons is of little credit or advantage to Science, to the nation, or to themselves.

The Micro-Organisms of Fermentation practically considered. By Alfred Jörgensen. Edited from the German by G. Harris Morris, Ph.D., F.C.S., F.I.C. With an Introduction by Horace T. Brown, F.C.S., F.I.C. London: F. W. Lyon.

The Carlsberg Laboratory, founded and endowed by the late eminent Danish brewer, J. C. Jacobsen, has become the seat of most important researches in the chemistry—or we had better say the chemico-biology—of fermentation. From it have emanated the studies of Dr. E. C. Hansen, which have marked a turning-point in the industry of brewing, and subsequently of Dr. Jörgensen, the author of the work before us.

In the Introduction an objection is very justly raised against the term bacteriology as applied to a study of the action of microbia upon organic matter. Those organisms with which the brewer and the manufacturers of wine and vinegar are chiefly concerned are not bacteria. At the same time the study of these ferments, as taken up by Pasteur, has been the starting point of this branch of biology. It is also pointed out in this Introduction as a result established by the labours of Hansen that the "supposed morphological differences which have been relied on to establish the various species and varieties of

the *Saccharomycetes* are in the highest degree illusory and untrustworthy; in fact, that species having very different physiological functions may assume forms which it is impossible to distinguish by a mere microscopical examination."

We have had recent proof of the importance of this variation in function, since it has been found that the different aroma of wines depends less on the species of grape, or soil, or climate than on the variety *Saccharomyces ellipsoideus*, otherwise known as *Mycoderma vini*.

Bacteria, as distinguished from the *Saccharomyces*, have an injurious effect alike in the production of wine, beer, and vinegar. The author lays great emphasis on the preparation of pure ferments, the methods for which are mainly due to Hansen. Those methods and the consequent improvements are not, as the author shows, restricted to bottom-yeast, but can be extended also to top-yeast, as used in English breweries. The instructions for the performance of experiments with the micro-organisms are admirably clear and full. The author calls attention to unfortunate mistakes which have been committed, and shows how the like may in future be avoided. Concerning disinfectants and sterilisers he reminds the reader that even mercuric chloride in dilute solutions is not so certainly and rapidly effective as it has been supposed. A solution of 1 in 300 is needed to stop the growth of some *Schizomycetes*.

Appended to the work is a copious bibliography of the subject.

English brewers ought to feel themselves much indebted to Dr. G. H. Morris for placing Jörgensen's work within their reach.

CORRESPONDENCE.

PENDULUM EXPERIMENTS AND GRAVITATION.

To the Editor of the Chemical News.

Sir,—It may be interesting to Mr. Thompson to know that the deviations of which he gives an account in the Chem. News (vol. lx., p. 295), are many thousand times as great as any that can be due to gravitation alone. While they may be interesting, as showing to what a great extent magnetism, electrification, convection currents, or tilting may give rise to spurious deflections, they cannot have any bearing on the question of gravitation or its cause.—I am, &c.,

C. V. Boys.

CHEMICAL NOTICES FROM FOREIGN SOURCES.

Note.—All degrees of temperature are Centigrade unless otherwise expressed.

Comptes Rendus Hebdomadaires des Séances, de l'Académie des Sciences. Vol. cix., No. 24, December 9, 1889.

The Nitrification of Ammonia.—Th. Schlœsing.—The author concludes that the nitrites are not merely products of an obstructed and incomplete nitrification, but they are in themselves an obstacle to the normal function of the nitrifying organisms. When nitrites are present there is a distinct escape of gaseous nitrogen. It does not, however, follow that the nitrites are the cause of the escape of nitrogen. It may be that the escape of the nitrogen and the presence of nitrites are merely simultaneous, and both due to one and the same cause. The destruction of nitrites in reducing media furnishes, according to the nature of such media, nitrous acid, nitrous and nitric oxide, free nitrogen, and even ammonia. Reciprocally he conceives that an incomplete oxidation of ammonia or of organic nitrogen yields merely free nitrogen or nitrous acid, or both simultaneously.

Combinations of Potassium and Sodium with Gaseous Ammonia.—A. Joannis.—It has been previously proved by Gore that potassium and sodium are capable of dissolving in liquefied ammoniacal gas. This liquid, as the gas escapes, deposits a solid body of a deeper red than copper. In this manner the author obtains solid sodammonium or potassammonium. The author is engaged with the further study of these bodies.

Ammoniacal Mercury Cyanides.—R. Varet.—The action of ammonia upon mercuric cyanide yields the two compounds $Hg_2Cy_2,2NH_3$ and $Hg_2Cy_2NH_3$. On operating in an aqueous solution and crystallising below 0° we obtain their hydrates.

Simultaneous Determination of Sulphur and Carbon in Organic Substances containing Sulphur.—L. Prunier.—This paper will be inserted in full.

An Isomer of Carballylic Acid.—E. Guinochet.—The acid obtained is certainly an isomer of the carballylic acid hitherto known, as is found by its composition, its physical properties, its capacity of saturation by bases, and its calcium and barium salts.

Two New Sugars obtained from Quebracho.—C. Tanret.—One of these, obtained directly, has been named quebrachite, and has the composition $C_{14}H_{14}O_{12}$. It does not ferment with beer-yeast. It is lævo-rotatory, and does not react on Fehling's solution. On splitting up it yields a lævo-rotatory inosite.

Researches on Carotine, and its Probable Physiological Function in Leaves.—M. Arnaud.—The author has determined the proportion of carotine in a considerable number of plants, and suggests that, like the hæmoglobine of blood, its function depends on its avidity for oxygen.

Bulletin de la Société Chimique de Paris. Series 3, Vol. ii., No. 9.

Action of Water on Stannic Chloride.—Leo Vignon.—When stannic chloride and water are mixed we obtain a solution of stannic oxide in dilute hydrochloric acid. This stannic oxide, which is very unstable, tends to become polymerised. In time the polymerisation reaches a certain state of equilibrium, which is a function of the dilution, the temperature, and the chemical composition of the liquid.

Methods of Analysis of the Feed-Waters of Steam-Boilers, with a View to the Use of Anti-Incrustation Agents.—Leo Vignon.—The author, approving of the proposal to use sodium carbonate as a de-incrustation agent, recommends a method for ascertaining the quantity needed. His reagents are saturated lime-water, which should be pure, and which contains, per litre, 1·80 grms. of $Ca(OH)_2$; a concentrated alcoholic solution of phenolphthalein, obtained by dissolving 5 grms. of neutral phenolphthalein in 100 c.c. of alcohol at 93°. A solution of calcium chloride, thoroughly neutral, containing about 5 grms. per cent. A solution of sodium carbonate containing 1 grm. sodium carbonate in 1 litre distilled water. For determining the carbonic acid he places in a stoppered test-jar 50 c.c. of distilled water and 10 drops of the alcoholic solution of phenolphthalein. In another test-jar he places 50 c.c. of the water in question, 10 drops of the solution of phenolphthalein, and 5 c.c. of the solution of calcium chloride. The first jar is then coloured by means of 0·2 to 0·5 c.c. of lime-water measured in with a burette. The colouration produced by the lime-water will disappear very rapidly at first, on agitation, so long as the carbonic acid in the liquid is in sufficient excess. Towards the end of the reaction the combination of the lime with the

carbonic acid is slower, whence the liquid must be frequently added, and the lime-water is added at longer intervals. When the colouration of the water under examination reaches and retains that of the standard—which may require an hour—the standard is made up with distilled water to the same volume as the water under examination, and lime-water is added to the less highly-coloured liquids, so as to equalise the tints; the two test-jars are then compared colorimetrically, and if examined against a white background, differences due to the presence of 0·1 c.c lime-water are easily detected. When the colourations are identical the two liquids contain the same quantity of free lime. The difference between the lime consumed by the standard liquid and the water under examination represents the quantity of lime absorbed by the free carbonic acid or that half-combined. To find the quantity of sodium carbonate which must be added to a boiler to prevent incineration, it is necessary to know the quantity of free or half-combined carbonic acid contained in 1 litre of the feed-water, and the quantity of sodium carbonate requisite to convert the calcium chloride and sulphate into insoluble carbonates.

Formation of Chloro-benzenes by the Superchloridation of Anisol.—L. Hugounenq.—This paper does not admit of useful abstraction.

Journal fur Praktische Chemie.
New Series, Vol. xl., 1889, Nos. 14 and 15.

The Action of Tin Salt upon Diazo-hydrocarbonates and Some Reactions of Diazoimido-hydrocarbons.—C. Culman and K. Gasiorowski.—This memoir does not admit of useful abstraction.

New Apparatus for Electro-chemical Investigations.—N. von Klobukow.—The author describes and figures stirring-arrangements in electro-chemical apparatus.

Calorimetric Researches by F. Stohmann.—Researches on the thermic value of carbon-acids of the aromatic series.

On Oriental Enamels on Tiles and on their Imitation.—J. Boeck.—The author compares the permanence of the enamels to be found in the Royal Mosque of Ispahan, built by Abbas the Great at the beginning of the 17th century, and those of the Alhambra, dating from the beginning of the 13th century, with the brief duration of external enamel work in Northern Europe, and admits that climate is, to a great extent, the cause of the difference. He gives the composition of a turquoise-blue enamel from the Mosque Schach Zende, built by Timur, as—

SiO_2	53·53
CuO	3·51
PbO	17·90
CaO	3·00
MgO	0·33
SnO_2	6 86
K_2O	3·51
Na_2O	7·27
Fe_2O_3, Al_2O_3	3·11
	99·02

and traces of As and Mn. He considers that there are only two possibilities of producing weather-proof enamelled tiles; either the clay must be burnt very compact, or its pores must be filled up in some manner so as to exclude the action of moisture and frost.

On the Regularities in the Apposition of Haloid Compounds on Non-saturated Acids.—A. Michael.—The author concludes that in organic compounds of the fatty series which contain several hydroxyls, that hydroxyl is first replaced by halogens, which is united with the relatively most positive carbon, or as it may be otherwise expressed, the hydroxyl of the most basic carbinol. In organic compounds which contain several symmetrically arranged atoms of the same halogen, that halogen is first replaced by another atom or a group, which is united with the most negative carbon. In the apposition of halogens and hydrocyanogens to the oxides of polyvalent organic radicles, the halogen and the cyanogen pass to the most positive carbon. If a reagent adds itself to an unsaturated and non-halogenous compound of the fatty series, its negative part goes to that unsaturated carbon which is relatively the most positive. In the addition of hydrohalogens to non-saturated acids of the fatty series, the halogen combines exclusively with the unsaturated carbon which is relatively the most positive.

MISCELLANEOUS.

An Appeal.—Mr. A. McDonald Graham died about two years ago, after a long illness, leaving a widow and several children quite without means of support. Mrs. Graham has had an operation, which restored somewhat her failing eyesight, but since the operation she has suffered from erysipelas, and is completely prostrated and in actual want. Donations may be made to Messrs. May and Baker, Garden Wharf, Battersea, London.

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MEETINGS FOR THE WEEK.

Tuesday, Dec. 31st.—Royal Institution, 3. "Electricity," by Prof. A. W. Rücker, F.R.S.
Thursday, Jan. 2nd.—Royal Institution, 3. "Electricity," by Prof. A. W. Rücker, F.R.S.
Friday, 3rd.—Geologists' Association, 8.
Saturday, 4th.—Royal Institution, 3. "Electricity," by Professor A. W. Rücker, F.R.S.

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